

SULFONIUM SALT

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Abstract of JP9012537

PURPOSE: To obtain a new sulfonium salt having an acid unstable group at the 3-site of the phenyl group of the sulfonium salt and useful as a component of a chemical amplification positive resist material suitable for fine processing technology. **CONSTITUTION:** This sulfonium salt is expressed by formula I ($R<1>$ is H, an alkyl, etc.; $OR<2>$ is an acid unstable group; Y is an alkylsulfonate, etc.; n is 0, 1 or 2; m is 1, 2 or 3; $n+m=3$), e.g. trifluoromethanesulfonic acid tris(3-t-butoxyphenyl)sulfonium salt. The exemplified substance of the compound of formula I having t-butyl group at the 3-site of the phenyl group and expressed by formula V can be produced by reacting a sulfoxide compound of formula II with a trialkylsilyl sulfonate compound of formula III ($R<3>$ is methyl or t-butyl) and further reacting with a Grignard reagent of formula IV (X is Br, etc.).

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CLAIMS

[Claim(s)]

[Claim 1] Sulfonium salt characterized by being shown by the following general formula (1) and having at least one acid unstable radical in the 3rd place of the phenyl group in a molecule.

[Formula 1]

(However, the inside R1 of a formula is a hydrogen atom, an alkyl group, an alkoxy group, or a dialkylamino radical, OR2 is an acid unstable radical and Y is a permutation, unsubstituted alkyl sulfonate, or aryl sulfonate.) n is the integer of 0-2, and m is the integer of 1-3, and the sum of n and m is 3.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to new sulfonium salt suitable as a component of the chemistry magnification positive-resist ingredient suitable for ultra-fine processing technology.

[0002]

[Description of the Prior Art] While detailed-ization of a pattern rule is called for with high integration and high-speed-izing of LSI, promising ** of the far-ultraviolet-rays lithography is carried out as next-generation ultra-fine processing technology. Far-ultraviolet-rays lithography is possible also for 0.3-0.4-micrometer processing, and the pattern formation with a perpendicularly near side attachment wall of it becomes [as opposed to / when the low resist ingredient of light absorption is used / a

substrate] possible. moreover -- as the light source of recent years and far ultraviolet rays -- high -- the technique of using a brightness KrF excimer laser attracts attention, in order to use this as mass production technology, light absorption is low and the high sensitivity resist ingredient is demanded.

[0003] Sensibility, resolution, and dry etching resistance are high, and the chemistry magnification positive-resist ingredients (JP,2-27660,B, JP,63-27829,A, etc.) which made the catalyst the acid developed in recent years from such a viewpoint have the outstanding description, and are resist ingredients especially promising for far-ultraviolet-rays lithography.

[0004] In this case, in the chemistry magnification positive-resist ingredient, it is known that the acid generator to blend will have big effect on the function as a chemistry magnification positive-resist ingredient especially. The onium salt shown below is mentioned as a typical thing of such an acid generator.

[0005]

[Formula 2]

[0006] The above-mentioned onium salt has the effectiveness of suppressing the film decrease at the time of development while it will reduce the solubility to the alkali water solution of a resist ingredient if it is blended as a resist component since itself is an oil solubility compound.

[0007] However, since it is the decomposition product mist beam oil solubility which in the case of a positive-resist ingredient is generated when an acid generator absorbs a high energy line, this decomposition product cannot reduce the dissolution rate to the alkali water solution of the exposure section, and cannot enlarge the alkali dissolution rate ratio (it is called dissolution contrast) of the exposure section and an unexposed part. For this reason, the chemistry magnification positive-resist ingredient using the above-mentioned onium salt had the fault of definition being low, and a pattern configuration having not become a rectangle but becoming the forward tapered shape of trapezoidal shape on the occasion of alkali development since the omission nature of the exposure section is bad.

[0008] Then, in order to solve this problem, introduce into the p-th place of a triphenylsulfonium salt the tert-butoxy radical which is an acid unstable radical, the phenol derivative which has alkali solubility in an operation of the acid disassembled and generated by high energy line exposure is made to generate, and enlarging dissolution contrast is performed (refer to Japanese Patent Application No. No. 317626 [six to]). However, even if it used the sulfonium salt which produces such a phenol

derivative, when it exposed on a substrate with a low reflection factor, it was difficult to obtain what is satisfied in respect of resolution.

[0009] This has the low transmission near 250nm of the above-mentioned sulfonium salt, and in order to reduce the permeability as resist film, when it exposes using a substrate with a low reflection factor, the optical reinforcement in the resist film upper part and the lower part differs, a difference appears in the yield of an acid, and it is considered for reducing definition.

[0010] Moreover, the conventional chemistry magnification positive-resist ingredient If the neglect time amount from exposure to PEB (Post Exposure Bake) becomes long when far ultraviolet rays, an electron ray, and X ray lithography are performed When pattern formation is carried out, the Rhine pattern becomes T-top configuration, namely, there is a problem [referred to as PED (PostExposure Deley)] that the pattern upper part becomes thick. This is considered for the solubility of a resist film front face to fall, and serves as a big fault in the case of presenting practical use. For this fault, the conventional chemistry magnification positive-resist ingredient [reference W.Hinsberg, et.al. and J.Photopolym.Sci.Technol. with the problem of spoiling dimension control even if it makes dimension control at a lithography process difficult and faces substrate processing using dry etching, 6 (4), 535-546(1993)., T.Kumada, et.al., J.Photopolym.Sci.Technol., and 6(4)571-574(1993). --] . This problem is solved and there is still no satisfying chemistry magnification positive-resist ingredient.

[0011] In the chemistry magnification positive-resist ingredient, the cause of the problem of PED is considered that the basic compound in air is involving greatly. The acid of a resist film front face generated by exposure reacts [the basic compound in air, and], and deactivates, and since the amount of the acid which deactivates so much will increase if the neglect time amount to PED becomes long, decomposition of an acid unstable radical stops being able to happen easily. Therefore, a refractory-ized layer is formed in a front face, and a pattern serves as T-top configuration.

[0012] In addition, since the effect of the basic compound in air can be suppressed by adding a basic compound in this case, it is known that there is effectiveness also in PED -- **** (JP,5-232706,A, 5-249683 official report, etc.) -- the basic compound used here according to examination of this invention person It turned out that are not incorporated by volatilization in the resist film, or compatibility with each component of a resist ingredient is bad, a problem is in the repeatability of effectiveness since distribution in the resist film is uneven, and definition is moreover dropped.

[0013] Therefore, development of the new component which gives the chemistry magnification positive-resist ingredient of high performance without the

above-mentioned problem is desired.

[0014] This invention was made in view of the above-mentioned situation, and aims at offering new sulfonium salt suitable as a component of the chemistry magnification positive-resist ingredient which has the high definition suitable for ultra-fine processing technology.

[0015]

[Means for Solving the Problem and its Function] this invention person makes the trialkylsilyl sulfonate shown by the diaryl sulfoxide shown by the following general formula (2) like the following reaction formula, and the following general formula (3) as a result of repeating examination wholeheartedly, in order to attain the above-mentioned purpose react. Furthermore, by making the GURINIYA reagent shown by the following general formula (4) which can be prepared at the reaction of 3-tert-butoxy phenyl chloride and metal magnesium react It found out that the new sulfonium salt which has a tert-butoxy radical in the 3rd place of the phenyl group shown by the following general formula (1a) was obtained. Furthermore, deprotection of the tert-butoxy radical of the sulfonium salt shown by this following general formula (1a) is carried out with an acid. With a conventional method, a tert-butoxycarbonyl radical, a tert-butoxy carbonylmethyl radical, By making the acid unstable radical which consists of a trialkylsilyl group, a tetrahydropyranyl group, a methoxymethyl radical, etc. permute by the 3rd place of a phenyl group The following new-type (1) sulfonium salt which has at least one acid unstable radical in the 3rd place of a phenyl group is obtained. It was suitable as a component of the chemistry magnification positive-resist ingredient which has the high definition to which the sulfonium salt of this above-mentioned formula (1) fitted ultra-fine processing technology, and found out that power could greatly be demonstrated especially in far-ultraviolet-rays lithography.

[0016]

[Formula 3]

(However, for the inside R1 of a formula, it is a hydrogen atom, an alkyl group, an alkoxy group, or a dialkylamino radical, OR2 is an acid unstable radical, and R3 is a methyl group or tert-butyl.) Y is a permutation, unsubstituted alkyl sulfonate, or aryl sulfonate. n is the integer of 0-2, and m is the integer of 1-3, and the sum of n and m is 3.

[0017] Namely, the sulfonium salt of the above-mentioned formula (1) of this invention Although the alkali solubility of the compound itself is low, they are the moisture in the acid generated by decomposition by high energy line exposure, and a resist ingredient, and an operation of PEB (Post Exposure Bake). An acid unstable radical decomposes

efficiently, and since a carboxylic acid part generates when it has the third class carboxylate radical like the high phenol part of alkali solubility, or a tert-butoxycarbonyl methyloxy radical, bigger dissolution contrast can be acquired.

[0018] Therefore, the sulfonium salt of the above-mentioned formula (1) can demonstrate the engine performance which was excellent as an acid generator of a chemistry magnification positive-resist ingredient. The resist ingredient containing the sulfonium salt of the above-mentioned formula (1) When it has big dissolution contrast and the light source near 250nm is especially used according to the effectiveness of the acid unstable radical of the sulfonium salt of the above-mentioned formula (1) By permuting the oxygen atom by the 3rd place which cannot take a sulfur atom and resonating structure, it is possible to raise the permeability near 250nm with a non-permuted thing more than equivalent, and, so, the resist image which has high resolution and the wide range depth of focus can be acquired.

[0019] That is, this invention is shown by the (A) following general formula (1), and the sulfonium salt characterized by having at least one acid unstable radical in the 3rd place of the phenyl group in a molecule is offered.

[0020]

[Formula 4]

(However, the inside R1 of a formula is a hydrogen atom, an alkyl group, an alkoxy group, or a dialkylamino radical, OR2 is an acid unstable radical and Y is a permutation, unsubstituted alkyl sulfonate, or aryl sulfonate.) n is the integer of 0-2, and m is the integer of 1-3, and the sum of n and m is 3.

[0021] Hereafter, when it explains per this invention and also to a detail, the new sulfonium salt of this invention is shown by the following general formula (1), and has at least one acid unstable radical in the 3rd place of the phenyl group in a molecule.

[0022]

[Formula 5]

(However, the inside R1 of a formula is a hydrogen atom, an alkyl group, an alkoxy group, or a dialkylamino radical, OR2 is an acid unstable radical and Y is a permutation, unsubstituted alkyl sulfonate, or aryl sulfonate.) n is the integer of 0-2, and m is the integer of 1-3, and the sum of n and m is 3.

[0023] In the above-mentioned formula (1), R1 is a hydrogen atom, an alkyl group, an alkoxy group, or a dialkylamino radical, the thing of the carbon numbers 1-8, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, sec-butyl, tert-butyl, a hexyl group, and a cyclohexyl radical, is concretely suitable for it as an

alkyl group, and a methyl group, an ethyl group, an isopropyl group, and tert-butyl are used more preferably especially. As an alkoxy group, the thing of the carbon numbers 1-8, such as a methoxy group, an ethoxy radical, a propoxy group, an isopropoxy group, an n-butoxy radical, a sec-butoxy radical, a tert-butoxy radical, a HEKISHIROKISHI radical, and a SHIKUROHEKI siloxy radical, is suitable, and a methoxy group, an ethoxy radical, an isopropoxy group, and a tert-butoxy radical are used more preferably especially. Although the amino group which has the alkyl group of the carbon numbers 1-4, such as a dimethylamino radical, a diethylamino radical, and a dipropylamino radical, is used as a dialkylamino radical, a dimethylamino radical is desirable especially.

[0024] OR2 is an acid unstable radical. Here, as an acid unstable radical, acetals, such as trialkylsilyloxy radicals, such as the third class carboxylate radicals, such as carbonate radicals, such as the third class alkoxy groups, such as a tert-butoxy radical, and a tert-butoxycarbonyloxy radical, and a tert-butoxycarbonyl methyloxy radical, a trimethylsilyloxy radical, a triethyl silyloxy radical, and a tert-butyl dimethylsilyloxy radical, a tetrahydropyranyloxy radical, a methoxymethyloxy radical, and an ethoxy ethyloxy radical, or a ketal radical is mentioned, for example.

[0025] Moreover, Y is a permutation, unsubstituted alkyl sulfonate, or aryl sulfonate, for example, trifluoromethane sulfonate, nonafluorobutane sulfonate, and p-toluene sulfonate are suitable for it. n is the integer of 0-2, and m is the integer of 1-3, and the sum of n and m is 3.

[0026] In addition, if the sulfonium salt which has a p-toluenesulfonic-acid anion (p-toluene sulfonate) in a counter anion (Y-) is used as a component of a resist ingredient especially in this invention Since effect of deactivation of an acid with the basic compound in air, the effectiveness, i.e., the resist film front face, of the p-toluenesulfonic-acid anion, can be made very small, Formation of a surface refractory layer can be suppressed, and it is good, and PED stability can fully solve the problem of the surface refractory layer which caused T-top configuration, i.e., the problem of PED, and can obtain better sensibility.

[0027] As sulfonium salt of such an above-mentioned formula (1), the following are illustrated concretely. namely, as sulfonium salt which has a tert-butoxy radical as an acid unstable radical For example, trifluoro methansulfonic acid (3-tert-butoxy phenyl) diphenyl sulfonium, P-toluenesulfonic-acid (3-tert-butoxy phenyl) diphenyl sulfonium, Nonafluorobutane sulfonic-acid (3-tert-butoxy phenyl) diphenyl sulfonium, Trifluoro methansulfonic acid bis(3-tert-butoxy phenyl) phenyl sulfonium, P-toluenesulfonic-acid bis(3-tert-butoxy phenyl) phenyl sulfonium, Nonafluorobutane sulfonic-acid bis(3-tert-butoxy phenyl) phenyl sulfonium, Trifluoro methansulfonic acid tris

(3-tert-butoxy phenyl) sulfonium, P-toluenesulfonic-acid tris (3-tert-butoxy phenyl) sulfonium, Nonafluorobutane sulfonic-acid tris (3-tert-butoxy phenyl) sulfonium, Trifluoro methansulfonic acid (3-tert-butoxy phenyl) bis(4-dimethylamino phenyl) sulfonium, P-toluenesulfonic-acid (3-tert-butoxy phenyl) bis(4-dimethylamino phenyl) sulfonium, Nonafluorobutane sulfonic-acid (3-tert-butoxy phenyl) bis(4-dimethylamino phenyl) sulfonium, Trifluoro methansulfonic acid bis(3-tert-butoxy phenyl) (4-dimethylamino phenyl) sulfonium, P-toluenesulfonic-acid bis(3-tert-butoxy phenyl) (4-dimethylamino phenyl) sulfonium, nonafluorobutane sulfonic-acid bis(3-tert-butoxy phenyl) (4-dimethylamino phenyl) sulfonium, etc. are mentioned.

[0028] As sulfonium salt which has a tert-butoxycarbonyloxy radical as an acid unstable radical Trifluoro methansulfonic acid bis(3-tert-butoxycarbonyloxy phenyl) phenyl sulfonium, P-toluenesulfonic-acid bis(3-tert-butoxycarbonyloxy phenyl) phenyl sulfonium, Trifluoro methansulfonic acid tris (3-tert-butoxycarbonyloxy phenyl) sulfonium, P-toluenesulfonic-acid tris (3-tert-butoxycarbonyloxy phenyl) sulfonium, Nonafluorobutane sulfonic-acid tris (3-tert-butoxycarbonyloxy phenyl) sulfonium, Trifluoro methansulfonic acid (3-tert-butoxycarbonyloxy phenyl) bis(4-dimethylamino phenyl) sulfonium, P-toluenesulfonic-acid (3-tert-butoxycarbonyloxy phenyl) bis(4-dimethylamino phenyl) sulfonium, Trifluoro methansulfonic acid bis(3-tert-butoxycarbonyloxy phenyl) (4-dimethylamino phenyl) sulfonium, P-toluenesulfonic-acid bis(3-tert-butoxycarbonyloxy phenyl) (4-dimethylamino phenyl) sulfonium, Nonafluorobutane sulfonic-acid bis(3-tert-butoxycarbonyloxy phenyl) (4-dimethylamino phenyl) sulfonium etc. is mentioned.

[0029] As sulfonium salt which has a tert-butoxycarbonyl methyloxy radical as an acid unstable radical Trifluoro methansulfonic acid bis(3-tert-butoxycarbonyl methyloxy phenyl) phenyl sulfonium, P-toluenesulfonic-acid bis(3-tert-butoxycarbonyl methyloxy phenyl) phenyl sulfonium, Trifluoro methansulfonic acid tris (3-tert-butoxycarbonyl methyloxy phenyl) sulfonium, Nonafluorobutane sulfonic-acid tris (3-tert-butoxycarbonyl methyloxy phenyl) sulfonium, Trifluoro methansulfonic acid (3-tert-butoxycarbonyl methyloxy phenyl) bis(4-dimethylamino phenyl) sulfonium, P-toluenesulfonic-acid bis(3-tert-butoxycarbonyl methyloxy phenyl) (4-dimethylamino phenyl) sulfonium etc. is mentioned.

[0030] As sulfonium salt which has an acetal or a ketal radical as an acid unstable radical As a thing with a tetrahydropyranyl group, trifluoro methansulfonic acid bis(3-(2-tetrahydropyranyl)-oxy-phenyl) phenyl sulfonium, Trifluoro methansulfonic acid tris (3-(2-tetrahydropyranyl)-oxy-phenyl) sulfonium, Nonafluorobutane sulfonic-acid tris (3-(2-tetrahydropyranyl)-oxy-phenyl) sulfonium, Trifluoro methansulfonic acid (3-(2-tetrahydropyranyl)-oxy-phenyl) bis(4-dimethylamino phenyl) sulfonium, As what

p-toluenesulfonic-acid bis(3-(2-tetrahydropyranyl)-oxy-phenyl) (4-dimethylamino phenyl) sulfonium etc. is mentioned, and has a methoxymethyl radical Trifluoro methansulfonic acid bis(3-methoxymethyloxy phenyl) phenyl sulfonium, Trifluoro methansulfonic acid tris (3-methoxymethyloxy phenyl) sulfonium, Nonafluorobutane sulfonic-acid tris (3-methoxymethyloxy phenyl) sulfonium, Trifluoro methansulfonic acid (3-methoxymethyloxy phenyl) bis(4-dimethylamino phenyl) sulfonium, p-toluenesulfonic-acid bis(3-methoxymethyloxy phenyl) (4-dimethylamino phenyl) sulfonium, etc. are mentioned.

[0031] As sulfonium salt which has a trialkylsilyloxy radical as an acid unstable radical Trifluoro methansulfonic acid bis(3-trimethylsilyloxy phenyl) phenyl sulfonium, P-toluenesulfonic-acid bis(3-triethyl silyloxy phenyl) phenyl sulfonium, Trifluoro methansulfonic acid tris (3-trimethylsilyloxy phenyl) sulfonium, Nonafluorobutane sulfonic-acid tris (3-trimethylsilyloxy phenyl) sulfonium, Trifluoro methansulfonic acid (3-triethyl silyloxy phenyl) bis(4-dimethylamino phenyl) sulfonium, p-toluenesulfonic-acid bis(3-trimethylsilyloxy phenyl) (4-dimethylamino phenyl) sulfonium, etc. are mentioned.

[0032] The sulfonium salt of the above-mentioned formula (1) of this invention is compoundable with the following paths. That is, the 3-halogenation-tert-butoxy benzene shown by the following general formula (7) which is made to carry out condensation of the isobutene shown by 3-halogenation phenol first shown, for example by the following general formula (5) and the following general formula (6) with an acid, and is obtained is made to react with THF Nakakane group magnesium with a conventional method, and it considers as 3-tert-butoxy phenyl GURINIYA (GURINIYA reagent) shown by the following general formula (4). Next, the sulfonium salt which has a 3-tert-butoxy phenyl group as an acid unstable radical shown by the following general formula (1a) is compoundable by making the trialkylsilyl sulfonate shown by the following general formula (3) react to the sulfoxide shown by the following general formula (2) in an organic solvent, and making the GURINIYA reagent of the following formula (4) react further.

[0033]

[Formula 6]

(However, the inside R1, R2, R3, Y, m, and n of a formula is the same as that of the above respectively, and X is a bromine atom or a chlorine atom.)

[0034] In the above-mentioned reaction, the reaction of the isobutene of 3-halogenation phenol of the above-mentioned formula (5) and the above-mentioned formula (6) can be performed according to J. "the fourth edition of an experimental science lecture,

organic synthesis 2, p200, the edited by Chemical Society of Japan, Maruzen", and "Holcombe and T.Livinghouse J.Org.Chem., 111-115.51. (1986)." In this case, when making 3-halogenation phenol of the above-mentioned formula (5), and the isobutene of the above-mentioned formula (6) react, 3-halogenation phenol of a formula (5) is received in the isobutene of a formula (6). 1-10 mols, That of ** especially added at a rate of 0.01-0.05 mols 0.01-0.1 mols to 3-halogenation phenol of a formula (5) in addition by making strong acid, such as trifluoro methansulfonic acid, into a catalyst with the rate of 3-5 mols is desirable. Moreover, as for a reaction, it is desirable in organic solvents, such as a methylene chloride, to carry out in a -40--70 degree C temperature requirement for 0.5 to 4 hours.

[0035] moreover, as a sulfoxide of the above-mentioned formula (2) A diphenyl sulfoxide, the bis(3, 4-G tert-butoxy phenyl) sulfoxide shown by the following formula (2a), The bis(4-tert-butoxy phenyl) sulfoxide shown by the following formula (2b), It is desirable to use the bis(4-dimethylamino phenyl) sulfoxide shown by the following formula (2c), the bis(3-tert-butoxy phenyl) sulfoxide shown by the following formula (2d) which is the condensation product of the GURINIYA reagent of the above-mentioned formula (4) and a thionyl chloride.

[0036]

[Formula 7]

[0037] In addition, composition of these sulfoxides compound can be performed according to an approach given in Japanese Patent Application No. No. 26171 [six to].

[0038] For example, when obtaining the compound of the above-mentioned formula (2b), it can carry out by the approach of making a thionyl chloride react to p-tert-butoxy phenyl GURINIYA shown by the following formula (A).

[0039]

[Formula 8]

(X shows chlorine or a bromine atom.)

[0040] In this case, it is desirable to perform a reaction in a methylene chloride and the organic solvent of THF. Moreover, in case a thionyl chloride is made to react to a GURINIYA reagent, 1/6 - 1/2 mol of thionyl chlorides is preferably dropped at 1 / a rate of 3 - 1/2 mol to a GURINIYA reagent, and -78 degrees C - 70 degrees C of reaction conditions are -60 degrees C - 10 degrees C preferably, and drop time is 45 - 90 minutes preferably for 10 to 120 minutes. After reaction termination can obtain the purpose compound for a solvent layer with recrystallization or a column chromatography after rinsing, desiccation, and concentration.

[0041] New sulfonium salt with one 3-tert-butoxy phenyl group is compoundable with this invention by using sulfoxides, such as the above-mentioned formula (2a), (2b), (2c), or a diphenyl sulfoxide, as a raw material. Moreover, new sulfonium salt with three 3-tert-butoxy phenyl groups is compoundable by using the sulfoxide of the above-mentioned formula (2d) for a raw material.

[0042] Moreover, the new sulfonium salt with two 3-tert-butoxy phenyl groups is compoundable by making the aryl GURINIYA reagent indicated to be the bis(3-tert-butoxy phenyl) sulfoxide of the above-mentioned formula (2d) by the following formula (8), for example, phenyl GURINIYA, 4-tert-butoxy phenyl GURINIYA, 4-dimethylamino phenyl GURINIYA, etc. react.

[0043]

[Formula 9]

(The inside R1, R3, Y, X, m, and n of the above-mentioned formula is the same as that of the above respectively.)

[0044] In addition, when what has a tert-butoxy radical is used at least for the 2nd place and 2' like a bis(2, 4-G tert-butoxy phenyl) sulfoxide as a sulfoxide of the above-mentioned formula (2), the purpose compound cannot be obtained because of a solid trauma. It is also the same as when what has a tetrahydropyranyloxy radical at least in the 2nd place and 2' is used.

[0045] Moreover, in the synthesis method of the sulfonium salt by the reaction of the phenol or anisole which is the conventional technique, and a thionyl chloride, or a sulfoxide compound, it may differ from an alt.substitution product and the Para substitution product with the reagent used since there is an active site of a phenol with the ortho position and the two para positions, and especially a meta-substitution product cannot be obtained. Furthermore, since hydrogen chloride gas occurs in the system of reaction at this reaction, it is difficult to compound a compound with an acid unstable radical like tert-butoxy benzene in a raw material. On the other hand, by the approach of this invention, since only a meta-substitution product is obtained quantitatively, the GURINIYA reagent is used and the mineral salt of a magnesium chloride etc. only generates instead of being hydrogen chloride gas, decomposition of an acid unstable radical does not advance.

[0046] In addition, although the 3-tert-butoxy phenyl GURINIYA reagent was used for the raw material of a sulfoxide and sulfonium salt in the above-mentioned synthesis method, even if it uses the GURINIYA reagent which was made to react with metal magnesium and was prepared, the sulfonium salt of the above-mentioned formula (1) is compoundable [the hydroxyl group of 3-halogenation phenol is protected by the

protective group from which it can be desorbed with inactive and an acid, for example, a tetrahydropyranyl group, to a GURINIYA reagent, and].

[0047] Especially in the above-mentioned reaction, it is desirable it to be suitable to mix 1-5 mols of trialkylsilyl sulfonate of the above-mentioned formula (3) at a rate of 2-3 mols, and to add especially 1-5 mols of GURINIYA reagents of the above-mentioned formula (4) or the above-mentioned formula (8) at a rate of 2-3 mols to the sulfoxide of the above-mentioned formula (2) to the sulfoxide of the above-mentioned formula (2). Furthermore, as for these reactions, it is desirable under existence of organic bases, such as triethylamine and a pyridine, to carry out in organic solvents, such as THF and a methylene chloride, in order to prevent the desorption of the tert-butoxy radical by the acid impurity of the minute amount which exists in the trialkylsilyl sulfonate of the above-mentioned formula (3). In addition, although especially the reaction condition of these reactions is not restricted, it is desirable to consider as the reaction temperature of 0-10 degrees C.

[0048] Furthermore, in this invention, the new sulfonium salt shown by the following general formula (1) which has the acid unstable radical made into the purpose in the 3rd place of a phenyl group can be obtained by carrying out deprotection of the tert-butoxy radical of the sulfonium salt of the above-mentioned formula (1a) with an acid, and permuting the hydrogen atom of a phenolic hydroxyl group with a conventional method by acid unstable radicals, such as a tert-butoxycarbonyl radical, a tert-butoxy carbonylmethyl radical, a trialkylsilyl group, a tetrahydropyranyl group, and a methoxymethyl radical.

[0049]

[Formula 10]

(However, the inside R1, R2, Y, n, and m of the above-mentioned formula is the same as that of the above respectively.)

[0050] Thus, the new sulfonium salt of the above-mentioned formula (1) of this invention obtained It is what is suitably used as an acid generator of a chemistry magnification positive-resist ingredient. Although the sulfonium salt of this formula (1) can be blended as an acid generator and can be prepared as a chemistry magnification positive-resist ingredient of binary system (an organic solvent, alkali fusibility resin, acid generator) or three-component system (an organic solvent, alkali fusibility resin, an acid generator, lysis inhibition agent) It is suitable to prepare as a chemistry magnification positive-resist ingredient of three-component system especially.

[0051] in this case, if it is desirable that it takes the 0.5 to 15 section (the weight section and the following -- the same) for the 2 - 8 section and it does not fulfill the 0.5 sections to the alkali fusibility resin 100 weight section, there are few acid yields at the

time of exposure, sensibility and resolving power may be inferior, if the 15 sections are exceeded, the permeability of a resist may fall, and especially the loadings of the sulfonium salt of the above-mentioned formula (1) as an acid generator may be inferior in resolving power

[0052] In addition, although the operation of the resist ingredient with which the sulfonium salt of the above-mentioned formula (1) was blended, optical operation, etc. can adopt a well-known lithography technique and can perform it, especially its above-mentioned resist ingredient is the optimal to detailed patterning by 254-193nm far-ultraviolet light and the electron ray.

[0053]

[Effect of the Invention] The new sulfonium salt of the above-mentioned formula (1) of this invention By having introduced the acid unstable radical into the 3rd place of the phenyl group of the sulfonium salt which is an acid generator By being able to enlarge dissolution contrast of the exposure section and an unexposed part, introducing an oxygen atom into the 3rd [further] place, and having prevented from taking resonating structure of a sulfur atom Since the transmission near 250nm can be raised a non-permuted triphenyl phosphonium salt and more than equivalent and the transmission as a resist ingredient can be raised as a result, it is effective as a component of the chemistry magnification positive-resist ingredient which has the high definition suitable for ultra-fine processing technology.

[0054]

[Example] Although an example and the example of a comparison, and the example of combination are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example. In addition, each section in each example is the weight section.

[0055] [Example 1]

Synthetic bis(3-tert-butoxy phenyl) sulfoxide 17.8g (0.052 mols) of trifluoromethanesulfonic acid tris (3-tert-butoxy phenyl) sulfonium was dissolved in THF52g, and it cooled in the iced water bath. The reaction was riped for 30 minutes, triethylamine 5.3g (0.052 mols) having been added to this, and having been dropped, controlling trimethylsilyl trifluoromethane sulfonate 28.6g (0.13 mols) not to exceed 10 degrees C, and having used reaction temperature as 0-10 degrees C. It was dropped controlling the GURINIYA reagent which used 3-tert-butoxy chlorobenzene 24.0g (0.13 mols), metal magnesium 3.2g (0.13 mols), and THF40g for this solution, and was prepared with the conventional method not to exceed 10 degrees C. Furthermore, the reaction was riped for 30 minutes, having used reaction temperature as 0-10 degrees C. After adding 300g of ammonium-chloride water solutions to reaction mixture 20% and

performing a halt and liquid separation of a reaction, chloroform 300g was added to the organic layer. After rinsing an organic layer twice using 200g of water, reduced pressure distilling off of the solvent was carried out, and oily matter was obtained. When this oily matter was applied to the column chromatography (silica gel: an extract, chloroform-methanol), trifluoro methansulfonic acid tris (3-tert-butoxy phenyl) sulfonium of the yield of 10.5g (29% of yield) and 99% of purity was isolated.

[0056] The result of the nuclear-magnetic-resonance spectrum (NMR) of the obtained trifluoro methansulfonic acid tris (3-tert-butoxy phenyl) sulfonium, an infrared spectrum (IR), an elemental-analysis value, and an ultraviolet absorption spectrum (UV) is shown below. In addition, the value of the ultraviolet absorption spectrum of trifluoro methansulfonic acid triphenylsulfonium and trifluoro methansulfonic acid tris (4-tert-butoxy phenyl) sulfonium is also shown as an example of a comparison.

[0057]

[Formula 11]

(a) 1.25 Singlet 27H(b)7.05-7.06 Triplet 3H(c) (e)7.25-7.29 Multiplet 6H(d)7.51-7.57 Triplet 3HIR:(cm⁻¹) 2980, 1587, 1564, 1477, 1423, 1394, 1369, 1263, 1259, 1159, 1031, 933, 912, 638

Elemental-analysis value: (%) C₃₁H₃₉O₆S₂F₃ theoretical value C:59.2 H:6.2 analysis value C:59.1 H:6.1 [0058]

[Table 1]

[0059] [Example 2] Except using phenyl GURINIYA instead of 3-tert-butoxy phenyl GURINIYA of an example 1, when reacted like the example 1, trifluoro methansulfonic acid bis(3-tert-butoxy phenyl) phenyl sulfonium was obtained at 98% of purity, and 35% of yield.

[0060] [Example 3] Except using a diphenyl sulfoxide instead of the sulfoxide of an example 1, when reacted like the example 1, trifluoro methansulfonic acid (3-tert-butoxy phenyl) diphenyl sulfonium was obtained at 98% of purity, and 27% of yield.

[0061] [Example 4] Except using a bis(4-dimethylamino phenyl) sulfoxide instead of the sulfoxide of an example 1, when reacted like the example 1, trifluoro methansulfonic acid (3-tert-butoxy phenyl) bis(4-dimethylamino phenyl) sulfonium was obtained at 98% of purity, and 27% of yield.

[0062] [Example 5] Except using 4-dimethylamino phenyl GURINIYA instead of the GURINIYA reagent of an example 1, when reacted like the example 1, trifluoro methansulfonic acid bis(3-tert-butoxy phenyl) (4-dimethylamino phenyl) sulfonium was obtained at 98% of purity, and 33% of yield.

[0063] [Examples 6-10] ***** made to react like examples 1-5 and the sulfonium salt

which has p-toluenesulfonic acid in the respectively following counter anions were obtained except using the trimethylsilyl-p-toluene sulfonate (113-117 degrees C of boiling points, 0.5 - 0.6mmHg) obtained by making p-toluenesulfonic acid and trimethylsilyl chloride react with a conventional method instead of the trimethylsilyl trifluoromethane sulfonate used in the examples 1-5.

Example 6: p-toluenesulfonic acid tris (3-tert-butoxy phenyl) sulfonium 99% of purity 35% example 7 of yield: p-toluenesulfonic acid bis(3-tert-butoxy phenyl) phenyl sulfonium 99% of purity 28% Example 8 of Yield: p-toluenesulfonic acid (3-tert-butoxy phenyl) diphenyl sulfonium 99% of purity 25% example 9 of yield: p-toluenesulfonic acid (3-tert-butoxy phenyl) bis(4-dimethylamino phenyl) sulfonium 97% of purity The 31% example 10 of yield: P-toluenesulfonic acid bis(3-tert-butoxy phenyl) (4-dimethylamino phenyl) sulfonium 98% of purity 32% [0064] of yield [Examples 11-15] ***** made to react like examples 1-5 and the sulfonium salt which has a nonafluorobutane sulfonic acid in the respectively following counter anions were obtained except using the trimethylsilyl nonafluorobutane sulfonate obtained by making a nonafluorobutane sulfonic acid and trimethylsilyl chloride react with a conventional method instead of the trimethylsilyl trifluoromethane sulfonate used in the examples 1-5.

Example 11: nonafluorobutane sulfonic acid tris (3-tert-butoxy phenyl) sulfonium 99% of purity 31% example 12 of yield: nonafluorobutane sulfonic acid bis(3-tert-butoxy phenyl) phenyl sulfonium 99% of purity The 28% example 13 of yield : A nonafluorobutane sulfonic acid (3-tert-butoxy phenyl) diphenyl sulfonium 99% of purity The 18% example 14 of yield : A nonafluorobutane sulfonic acid (3-tert-butoxy phenyl) bis(4-dimethylamino phenyl) sulfonium 98% of purity 27% example 15 of yield: nonafluorobutane sulfonic acid bis(3-tert-butoxy phenyl) (4-dimethylamino phenyl) sulfonium 97% of purity 25% [0065] of yield [Examples 16-19] Deprotection of the new sulfonium salt which has the tert-butoxy radical obtained in the examples 1-15 in the 3rd place is carried out in a methanol or ethanol using the same sulfonic acid as a counter anion (for example, trifluoromethane sulfonate and p-toluene sulfonate). After obtaining corresponding 3-hydroxyphenyl sulfonium salt almost quantitatively, The sulfonium salt which has an acid unstable radical as shown below by using G tert-butyl-JIKARUBONETO or chloroacetic acid-tert-butyl, and a dihydropyran with a conventional method in the 3rd place of a phenyl group was compounded.

Example 16: NONARI fluoro butane sulfonic acid bis(3-tert-butoxycarbonyloxy phenyl) phenyl sulfonium 98% of purity, The 23% example 17 of yield: Trifluoro methanesulfonic acid (3-tert-butoxycarbonyl methoxyloxy phenyl) diphenyl sulfonium 98% of purity, The 25% example 18 of yield: P-toluenesulfonic acid

(3-tert-butoxycarbonyloxy phenyl) diphenyl sulfonium 98% of purity, The 19% example 19 of yield: Nonafluorobutane sulfonic-acid tris (3-tert-butoxycarbonyl methoxy phenyl) sulfonium 98% of purity, 18% [0066] of yield The molar extinction coefficient of an ultraviolet absorption spectrum [in / the 4th place / as a substitution product (3-tert-butoxy phenyl sulfonium salt) and an example of a comparison / the 3rd place / 248nm of a substitution product (4-tert-butoxy phenyl sulfonium salt)] of the new sulfonium salt of the above-mentioned examples 1-10 is shown in Table 2.

[0067] It turned out that the effectiveness shows up most greatly in tris (tert-butoxy phenyl) sulfonium salt with many tert-butoxy phenyl groups by the ability lessening 248nm light absorption when the sulfonium salt of this invention is not the 4th place and has a tert-butoxy radical in the 3rd place so that clearly from the result of Table 2.

[0068]

[Table 2]

[0069] [The examples 1-14 of combination and examples 1-5 of comparison combination] Polyhydroxy styrene which is shown by the following formula (Polym.1) as shown in Tables 3 and 4 and which protected the hydrogen atom of a hydroxyl group by the tert-BUTOSHIKI carbonyl group partially, The polyhydroxy styrene which is shown by the polyhydroxy styrene or the following type (Polym.3) which is shown by the following formula (Polym.2), and which protected the hydrogen atom of a hydroxyl group by tert-butyl partially and which protected the hydrogen atom of a hydroxyl group by the tetrahydropyranyl group partially, The acid generator chosen from the onium salt shown by (PAG.5) from the following type (PAG.1), The lysis inhibition agent of the 2 and 2'-bis(4-tert-butoxycarbonyloxy phenyl) propane shown by the following formula (Data Resources.1) was dissolved in 1-ethoxy-2-propanol, and the resist constituent of the various presentations shown in Table 3 was prepared.

[0070] After preparing resist liquid by filtering the obtained resist constituent with the 0.2-micrometer filter made from Teflon, spin coating of this resist liquid was carried out to up to the silicone wafer, and it applied to 0.8 micrometers.

[0071] Subsequently, BEKU [this silicone wafer / with the 100-degree C hot plate] for 120 seconds. Furthermore, when it exposed using the excimer laser stepper (NIKON CORP., NSR2005EXNA=0.5), BEKU during 60 seconds was given at 90 degrees C and negatives were developed in the water solution of 2.38% of tetramethylammonium hydroxide, the pattern of a positive type was able to be obtained.

[0072] The obtained resist pattern was evaluated as follows. A result is shown in Tables 3 and 4.

The resist-pattern evaluation approach: It asked for sensibility (Eth) first. Next, minimum line width of separated Rhine in this light exposure and a tooth space was

made into the resolution of an evaluation resist by making into the optimal light exposure (sensitivity: Eop) light exposure which resolves the top and the bottom of a 0.35-micrometer Rhine and a tooth space by 1:1. Moreover, the configuration of the resolved resist pattern was observed using the scanning electron microscope.

[0073]

[Formula 12]

[0074]

[Formula 13]

[0075]

[Table 3]

[0076]

[Table 4]

[0077] [the examples 15-28 of combination, and the examples 5-8 of comparison combination] -- it is shown in Tables 5 and 6 -- as -- as an acid generator -- the following (PAG.6-8) -- or -- having mentioned above (PAG 4 and 5) -- the positive type pattern was obtained like the above-mentioned example 1 of combination except using. In addition, the nitrogen content compound for PED stability was added to the example 28 of combination as an additive.

[0078] The obtained resist pattern was similarly estimated as the above. Furthermore, the PED stability of a resist changed after exposure and neglect time amount with the optimal light exposure, performed PEB, and the time amount by which change of a resist pattern configuration was observed, for example, the Rhine pattern, became T-top, and it evaluated it by time amount it became impossible to resolve. It is rich in PED stability, so that this time amount is long. The above result is shown in Tables 5 and 6.

[0079]

[Formula 14]

[0080]

[Table 5]

[0081]

[Table 6]

TECHNICAL FIELD

[Industrial Application] This invention relates to new sulfonium salt suitable as a component of the chemistry magnification positive-resist ingredient suitable for ultra-fine processing technology.

EFFECT OF THE INVENTION

[Effect of the Invention] The new sulfonium salt of the above-mentioned formula (1) of this invention By having introduced the acid unstable radical into the 3rd place of the phenyl group of the sulfonium salt which is an acid generator By being able to enlarge dissolution contrast of the exposure section and an unexposed part, introducing an oxygen atom into the 3rd [further] place, and having prevented from taking resonating structure of a sulfur atom Since the transmission near 250nm can be raised a non-permuted triphenyl phosphonium salt and more than equivalent and the transmission as a resist ingredient can be raised as a result, it is effective as a component of the chemistry magnification positive-resist ingredient which has the high definition suitable for ultra-fine processing technology.

TECHNICAL PROBLEM

[Description of the Prior Art] While detailed-ization of a pattern rule is called for with high integration and high-speed-izing of LSI, promising ** of the far-ultraviolet-rays lithography is carried out as next-generation ultra-fine processing technology. Far-ultraviolet-rays lithography is possible also for 0.3-0.4-micrometer processing, and the pattern formation with a perpendicularly near side attachment wall of it becomes [as opposed to / when the low resist ingredient of light absorption is used / a substrate] possible. moreover -- as the light source of recent years and far ultraviolet rays -- high -- the technique of using a brightness KrF excimer laser attracts attention, in order to use this as mass production technology, light absorption is low and the high sensitivity resist ingredient is demanded.

[0003] Sensibility, resolution, and dry etching resistance are high, and the chemistry magnification positive-resist ingredients (JP,2-27660,B, JP,63-27829,A, etc.) which made the catalyst the acid developed in recent years from such a viewpoint have the outstanding description, and are resist ingredients especially promising for far-ultraviolet-rays lithography.

[0004] In this case, in the chemistry magnification positive-resist ingredient, it is known that the acid generator to blend will have big effect on the function as a chemistry magnification positive-resist ingredient especially. The onium salt shown below is mentioned as a typical thing of such an acid generator.

[0005]

[Formula 2]

[0006] The above-mentioned onium salt has the effectiveness of suppressing the film decrease at the time of development while it will reduce the solubility to the alkali water solution of a resist ingredient if it is blended as a resist component since itself is an oil solubility compound.

[0007] However, since it is the decomposition product mist beam oil solubility which in the case of a positive-resist ingredient is generated when an acid generator absorbs a high energy line, this decomposition product cannot reduce the dissolution rate to the alkali water solution of the exposure section, and cannot enlarge the alkali dissolution rate ratio (it is called dissolution contrast) of the exposure section and an unexposed part. For this reason, the chemistry magnification positive-resist ingredient using the above-mentioned onium salt had the fault of definition being low, and a pattern configuration having not become a rectangle but becoming the forward tapered shape of trapezoidal shape on the occasion of alkali development since the omission nature of the exposure section is bad.

[0008] Then, in order to solve this problem, introduce into the p-th place of a triphenylsulfonium salt the tert-butoxy radical which is an acid unstable radical, the phenol derivative which has alkali solubility in an operation of the acid disassembled and generated by high energy line exposure is made to generate, and enlarging dissolution contrast is performed (refer to Japanese Patent Application No. No. 317626 [six to]). However, even if it used the sulfonium salt which produces such a phenol derivative, when it exposed on a substrate with a low reflection factor, it was difficult to obtain what is satisfied in respect of resolution.

[0009] This has the low transmission near 250nm of the above-mentioned sulfonium salt, and in order to reduce the permeability as resist film, when it exposes using a substrate with a low reflection factor, the optical reinforcement in the resist film upper part and the lower part differs, a difference appears in the yield of an acid, and it is considered for reducing definition.

[0010] Moreover, the conventional chemistry magnification positive-resist ingredient If the neglect time amount from exposure to PEB (Post Exposure Bake) becomes long when far ultraviolet rays, an electron ray, and X ray lithography are performed When pattern formation is carried out, the Rhine pattern becomes T-top configuration, namely, there is a problem [referred to as PED (PostExposure Deley)] that the pattern upper part becomes thick. This is considered for the solubility of a resist film front face to fall, and serves as a big fault in the case of presenting practical use. For this fault, the conventional chemistry magnification positive-resist ingredient [reference:W.Hinsberg, et.al. and J.Photopolym.Sci.Technol. with the problem of spoiling dimension control even if it makes dimension control at a lithography process

difficult and faces substrate processing using dry etching, 6 (4), 535-546(1993)., T.Kumada, et.al., J.Photopolym.Sci.Technol., and 6(4)571-574(1993). --] . This problem is solved and there is still no satisfying chemistry magnification positive-resist ingredient.

[0011] In the chemistry magnification positive-resist ingredient, the cause of the problem of PED is considered that the basic compound in air is involving greatly. The acid of a resist film front face generated by exposure reacts [the basic compound in air, and], and deactivates, and since the amount of the acid which deactivates so much will increase if the neglect time amount to PED becomes long, decomposition of an acid unstable radical stops being able to happen easily. Therefore, a refractory-ized layer is formed in a front face, and a pattern serves as T-top configuration.

[0012] In addition, since the effect of the basic compound in air can be suppressed by adding a basic compound in this case, it is known that there is effectiveness also in PED -- **** (JP,5-232706,A, 5-249683 official report, etc.) -- the basic compound used here according to examination of this invention person It turned out that are not incorporated by volatilization in the resist film, or compatibility with each component of a resist ingredient is bad, a problem is in the repeatability of effectiveness since distribution in the resist film is uneven, and definition is moreover dropped.

[0013] Therefore, development of the new component which gives the chemistry magnification positive-resist ingredient of high performance without the above-mentioned problem is desired.

[0014] This invention was made in view of the above-mentioned situation, and aims at offering new sulfonium salt suitable as a component of the chemistry magnification positive-resist ingredient which has the high definition suitable for ultra-fine processing technology.

OPERATION

[Means for Solving the Problem and its Function] this invention person makes the trialkylsilyl sulfonate shown by the diaryl sulfoxide shown by the following general formula (2) like the following reaction formula, and the following general formula (3) as a result of repeating examination wholeheartedly, in order to attain the above-mentioned purpose react. Furthermore, by making the GURINIYA reagent shown by the following general formula (4) which can be prepared at the reaction of 3-tert-butoxy phenyl chloride and metal magnesium react It found out that the new sulfonium salt which has a tert-butoxy radical in the 3rd place of the phenyl group shown by the following general formula (1a) was obtained. Furthermore, deprotection

of the tert-butoxy radical of the sulfonium salt shown by this following general formula (1a) is carried out with an acid. With a conventional method, a tert-butoxycarbonyl radical, a tert-butoxy carbonylmethyl radical, By making the acid unstable radical which consists of a trialkylsilyl group, a tetrahydropyranyl group, a methoxymethyl radical, etc. permute by the 3rd place of a phenyl group The following new-type (1) sulfonium salt which has at least one acid unstable radical in the 3rd place of a phenyl group is obtained. It was suitable as a component of the chemistry magnification positive-resist ingredient which has the high definition to which the sulfonium salt of this above-mentioned formula (1) fitted ultra-fine processing technology, and found out that power could greatly be demonstrated especially in far-ultraviolet-rays lithography. [0016]

[Formula 3]

(However, for the inside R1 of a formula, it is a hydrogen atom, an alkyl group, an alkoxy group, or a dialkylamino radical, OR2 is an acid unstable radical, and R3 is a methyl group or tert-butyl.) Y is a permutation, unsubstituted alkyl sulfonate, or aryl sulfonate. n is the integer of 0-2, and m is the integer of 1-3, and the sum of n and m is 3.

[0017] Namely, the sulfonium salt of the above-mentioned formula (1) of this invention Although the alkali solubility of the compound itself is low, they are the moisture in the acid generated by decomposition by high energy line exposure, and a resist ingredient, and an operation of PEB (Post Exposure Bake). An acid unstable radical decomposes efficiently, and since a carboxylic-acid part generates when it has the third class carboxylate radical like the high phenol part of alkali solubility, or a tert-butoxycarbonyl methyloxy radical, bigger dissolution contrast can be acquired.

[0018] Therefore, the sulfonium salt of the above-mentioned formula (1) can demonstrate the engine performance which was excellent as an acid generator of a chemistry magnification positive-resist ingredient. The resist ingredient containing the sulfonium salt of the above-mentioned formula (1) When it has big dissolution contrast and the light source near 250nm is especially used according to the effectiveness of the acid unstable radical of the sulfonium salt of the above-mentioned formula (1) By permuting the oxygen atom by the 3rd place which cannot take a sulfur atom and resonating structure, it is possible to raise the permeability near 250nm with a non-permuted thing more than equivalent, and, so, the resist image which has high resolution and the wide range depth of focus can be acquired.

[0019] That is, this invention is shown by the (A) following general formula (1), and the sulfonium salt characterized by having at least one acid unstable radical in the 3rd place of the phenyl group in a molecule is offered.

[0020]

[Formula 4]

(However, the inside R1 of a formula is a hydrogen atom, an alkyl group, an alkoxy group, or a dialkylamino radical, OR2 is an acid unstable radical and Y is a permutation, unsubstituted alkyl sulfonate, or aryl sulfonate.) n is the integer of 0-2, and m is the integer of 1-3, and the sum of n and m is 3.

[0021] Hereafter, when it explains per this invention and also to a detail, the new sulfonium salt of this invention is shown by the following general formula (1), and has at least one acid unstable radical in the 3rd place of the phenyl group in a molecule.

[0022]

[Formula 5]

(However, the inside R1 of a formula is a hydrogen atom, an alkyl group, an alkoxy group, or a dialkylamino radical, OR2 is an acid unstable radical and Y is a permutation, unsubstituted alkyl sulfonate, or aryl sulfonate.) n is the integer of 0-2, and m is the integer of 1-3, and the sum of n and m is 3.

[0023] In the above-mentioned formula (1), R1 is a hydrogen atom, an alkyl group, an alkoxy group, or a dialkylamino radical, the thing of the carbon numbers 1-8, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, sec-butyl, tert-butyl, a hexyl group, and a cyclohexyl radical, is concretely suitable for it as an alkyl group, and a methyl group, an ethyl group, an isopropyl group, and tert-butyl are used more preferably especially. As an alkoxy group, the thing of the carbon numbers 1-8, such as a methoxy group, an ethoxy radical, a propoxy group, an isopropoxy group, an n-butoxy radical, a sec-butoxy radical, a tert-butoxy radical, a HEKISHIROKISHI radical, and a SHIKUROHEKI siloxy radical, is suitable, and a methoxy group, an ethoxy radical, an isopropoxy group, and a tert-butoxy radical are used more preferably especially. Although the amino group which has the alkyl group of the carbon numbers 1-4, such as a dimethylamino radical, a diethylamino radical, and a dipropylamino radical, is used as a dialkylamino radical, a dimethylamino radical is desirable especially.

[0024] OR2 is an acid unstable radical. Here, as an acid unstable radical, acetals, such as trialkylsilyloxy radicals, such as the third class carboxylate radicals, such as carbonate radicals, such as the third class alkoxy groups, such as a tert-butoxy radical, and a tert-butoxycarbonyloxy radical, and a tert-butoxycarbonyl methyloxy radical, a trimethylsilyloxy radical, a triethyl silyloxy radical, and a tert-butyldimethylsilyloxy radical, a tetrahydropyranyloxy radical, a methoxymethyloxy radical, and an ethoxy ethyloxy radical, or a ketal radical is mentioned, for example.

[0025] Moreover, Y is a permutation, unsubstituted alkyl sulfonate, or aryl sulfonate,

for example, trifluoromethane sulfonate, nonafluorobutane sulfonate, and p-toluene sulfonate are suitable for it. n is the integer of 0-2, and m is the integer of 1-3, and the sum of n and m is 3.

[0026] In addition, if the sulfonium salt which has a p-toluenesulfonic-acid anion (p-toluene sulfonate) in a counter anion (Y-) is used as a component of a resist ingredient especially in this invention Since effect of deactivation of an acid with the basic compound in air, the effectiveness, i.e., the resist film front face, of the p-toluenesulfonic-acid anion, can be made very small, Formation of a surface refractory layer can be suppressed, and it is good, and PED stability can fully solve the problem of the surface refractory layer which caused T-top configuration, i.e., the problem of PED, and can obtain better sensibility.

[0027] As sulfonium salt of such an above-mentioned formula (1), the following are illustrated concretely. namely, as sulfonium salt which has a tert-butoxy radical as an acid unstable radical For example, trifluoro methansulfonic acid (3-tert-butoxy phenyl) diphenyl sulfonium, P-toluenesulfonic-acid (3-tert-butoxy phenyl) diphenyl sulfonium, Nonafluorobutane sulfonic-acid (3-tert-butoxy phenyl) diphenyl sulfonium, Trifluoro methansulfonic acid bis(3-tert-butoxy phenyl) phenyl sulfonium, P-toluenesulfonic-acid bis(3-tert-butoxy phenyl) phenyl sulfonium, Nonafluorobutane sulfonic-acid bis(3-tert-butoxy phenyl) phenyl sulfonium, Trifluoro methansulfonic acid tris (3-tert-butoxy phenyl) sulfonium, P-toluenesulfonic-acid tris (3-tert-butoxy phenyl) sulfonium, Nonafluorobutane sulfonic-acid tris (3-tert-butoxy phenyl) sulfonium, Trifluoro methansulfonic acid (3-tert-butoxy phenyl) bis(4-dimethylamino phenyl) sulfonium, P-toluenesulfonic-acid (3-tert-butoxy phenyl) bis(4-dimethylamino phenyl) sulfonium, Nonafluorobutane sulfonic-acid (3-tert-butoxy phenyl) bis(4-dimethylamino phenyl) sulfonium, Trifluoro methansulfonic acid bis(3-tert-butoxy phenyl) (4-dimethylamino phenyl) sulfonium, P-toluenesulfonic-acid bis(3-tert-butoxy phenyl) (4-dimethylamino phenyl) sulfonium, nonafluorobutane sulfonic-acid bis(3-tert-butoxy phenyl) (4-dimethylamino phenyl) sulfonium, etc. are mentioned.

[0028] As sulfonium salt which has a tert-buthoxycarbonyloxy radical as an acid unstable radical Trifluoro methansulfonic acid bis(3-tert-buthoxycarbonyloxy phenyl) phenyl sulfonium, P-toluenesulfonic-acid bis(3-tert-buthoxycarbonyloxy phenyl) phenyl sulfonium, Trifluoro methansulfonic acid tris (3-tert-buthoxycarbonyloxy phenyl) sulfonium, P-toluenesulfonic-acid tris (3-tert-buthoxycarbonyloxy phenyl) sulfonium, Nonafluorobutane sulfonic-acid tris (3-tert-buthoxycarbonyloxy phenyl) sulfonium, Trifluoro methansulfonic acid (3-tert-buthoxycarbonyloxy phenyl) bis(4-dimethylamino phenyl) sulfonium, P-toluenesulfonic-acid (3-tert-buthoxycarbonyloxy phenyl) bis(4-dimethylamino phenyl) sulfonium, Trifluoro methansulfonic acid

bis(3-tert-butoxycarbonyloxy phenyl) (4-dimethylamino phenyl) sulfonium, P-toluenesulfonic-acid bis(3-tert-butoxycarbonyloxy phenyl) (4-dimethylamino phenyl) sulfonium, Nonafluorobutane sulfonic-acid bis(3-tert-butoxycarbonyloxy phenyl) (4-dimethylamino phenyl) sulfonium etc. is mentioned.

[0029] As sulfonium salt which has a tert-butoxycarbonyl methyloxy radical as an acid unstable radical Trifluoro methansulfonic acid bis(3-tert-butoxycarbonyl methyloxy phenyl) phenyl sulfonium, P-toluenesulfonic-acid bis(3-tert-butoxycarbonyl methyloxy phenyl) phenyl sulfonium, Trifluoro methansulfonic acid tris (3-tert-butoxycarbonyl methyloxy phenyl) sulfonium, Nonafluorobutane sulfonic-acid tris (3-tert-butoxycarbonyl methyloxy phenyl) sulfonium, Trifluoro methansulfonic acid (3-tert-butoxycarbonyl methyloxy phenyl) bis(4-dimethylamino phenyl) sulfonium, P-toluenesulfonic-acid bis(3-tert-butoxycarbonyl methyloxy phenyl) (4-dimethylamino phenyl) sulfonium etc. is mentioned.

[0030] As sulfonium salt which has an acetal or a ketal radical as an acid unstable radical As a thing with a tetrahydropyranyl group, trifluoro methansulfonic acid bis(3-(2-tetrahydropyranyl)-oxy-phenyl) phenyl sulfonium, Trifluoro methansulfonic acid tris (3-(2-tetrahydropyranyl)-oxy-phenyl) sulfonium, Nonafluorobutane sulfonic-acid tris (3-(2-tetrahydropyranyl)-oxy-phenyl) sulfonium, Trifluoro methansulfonic acid (3-(2-tetrahydropyranyl)-oxy-phenyl) bis(4-dimethylamino phenyl) sulfonium, As what p-toluenesulfonic-acid bis(3-(2-tetrahydropyranyl)-oxy-phenyl) (4-dimethylamino phenyl) sulfonium etc. is mentioned, and has a methoxymethyl radical Trifluoro methansulfonic acid bis(3-methoxymethyloxy phenyl) phenyl sulfonium, Trifluoro methansulfonic acid tris (3-methoxymethyloxy phenyl) sulfonium, Nonafluorobutane sulfonic-acid tris (3-methoxymethyloxy phenyl) sulfonium, Trifluoro methansulfonic acid (3-methoxymethyloxy phenyl) bis(4-dimethylamino phenyl) sulfonium, p-toluenesulfonic-acid bis(3-methoxymethyloxy phenyl) (4-dimethylamino phenyl) sulfonium, etc. are mentioned.

[0031]-As sulfonium salt which has a trialkylsilyloxy radical as an acid unstable radical Trifluoro methansulfonic acid bis(3-trimethylsilyloxy phenyl) phenyl sulfonium, P-toluenesulfonic-acid bis(3-triethyl silyloxy phenyl) phenyl sulfonium, Trifluoro methansulfonic acid tris (3-trimethylsilyloxy phenyl) sulfonium, Nonafluorobutane sulfonic-acid tris (3-trimethylsilyloxy phenyl) sulfonium, Trifluoro methansulfonic acid (3-triethyl silyloxy phenyl) bis(4-dimethylamino phenyl) sulfonium, p-toluenesulfonic-acid bis(3-trimethylsilyloxy phenyl) (4-dimethylamino phenyl) sulfonium, etc. are mentioned.

[0032] The sulfonium salt of the above-mentioned formula (1) of this invention is compoundable with the following paths. That is, the 3-halogenation-tert-butoxy

benzene shown by the following general formula (7) which is made to carry out condensation of the isobutene shown by 3-halogenation phenol first shown, for example by the following general formula (5) and the following general formula (6) with an acid, and is obtained is made to react with THF Nakakane group magnesium with a conventional method, and it considers as 3-tert-butoxy phenyl GURINIYA (GURINIYA reagent) shown by the following general formula (4). Next, the sulfonium salt which has a 3-tert-butoxy phenyl group as an acid unstable radical shown by the following general formula (1a) is compoundable by making the trialkylsilyl sulfonate shown by the following general formula (3) react to the sulfoxide shown by the following general formula (2) in an organic solvent, and making the GURINIYA reagent of the following formula (4) react further.

[0033]

[Formula 6]

(However, the inside R1, R2, R3, Y, m, and n of a formula is the same as that of the above respectively, and X is a bromine atom or a chlorine atom.)

[0034] In the above-mentioned reaction, the reaction of the isobutene of 3-halogenation phenol of the above-mentioned formula (5) and the above-mentioned formula (6) can be performed according to J. "the fourth edition of an experimental science lecture, organic synthesis 2, p200, the edited by Chemical Society of Japan, Maruzen", and "Holcombe and T.Livinghouse J.Org.Chem., 111-115.51. (1986)." In this case, when making 3-halogenation phenol of the above-mentioned formula (5), and the isobutene of the above-mentioned formula (6) react, 3-halogenation phenol of a formula (5) is received in the isobutene of a formula (6). 1-10 mols, That of ** especially added at a rate of 0.01-0.05 mols 0.01-0.1 mols to 3-halogenation phenol of a formula (5) in addition by making strong acid, such as trifluoro methansulfonic acid, into a catalyst with the rate of 3-5 mols is desirable. Moreover, as for a reaction, it is desirable in organic solvents, such as a methylene chloride, to carry out in a -40--70 degree C temperature requirement for 0.5 to 4 hours.

[0035] moreover, as a sulfoxide of the above-mentioned formula (2) A diphenyl sulfoxide, the bis(3, 4-G tert-butoxy phenyl) sulfoxide shown by the following formula (2a), The bis(4-tert-butoxy phenyl) sulfoxide shown by the following formula (2b), It is desirable to use the bis(4-dimethylamino phenyl) sulfoxide shown by the following formula (2c), the bis(3-tert-butoxy phenyl) sulfoxide shown by the following formula (2d) which is the condensation product of the GURINIYA reagent of the above-mentioned formula (4) and a thionyl chloride.

[0036]

[Formula 7]

[0037] In addition, composition of these sulfoxides compound can be performed according to an approach given in Japanese Patent Application No. No. 26171 [six to].

[0038] For example, when obtaining the compound of the above-mentioned formula (2b), it can carry out by the approach of making a thionyl chloride react to p-tert-butoxy phenyl GURINIYA shown by the following formula (A).

[0039]

[Formula 8]

(X shows chlorine or a bromine atom.)

[0040] In this case, it is desirable to perform a reaction in a methylene chloride and the organic solvent of THF. Moreover, in case a thionyl chloride is made to react to a GURINIYA reagent, 1-6 - 1/2 mol of thionyl chlorides is preferably dropped at 1 / a rate of 3 - 1/2 mol to a GURINIYA reagent, and -78 degrees C - 70 degrees C of reaction conditions are -60 degrees C - 10 degrees C preferably, and drop time is 45 - 90 minutes preferably for 10 to 120 minutes. After reaction termination can obtain the purpose compound for a solvent layer with recrystallization or a column chromatography after rinsing, desiccation, and concentration.

[0041] New sulfonium salt with one 3-tert-butoxy phenyl group is compoundable with this invention by using sulfoxides, such as the above-mentioned formula (2a), (2b), (2c), or a diphenyl sulfoxide, as a raw material. Moreover, new sulfonium salt with three 3-tert-butoxy phenyl groups is compoundable by using the sulfoxide of the above-mentioned formula (2d) for a raw material.

[0042] Moreover, the new sulfonium salt with two 3-tert-butoxy phenyl groups is compoundable by making the aryl GURINIYA reagent indicated to be the bis(3-tert-butoxy phenyl) sulfoxide of the above-mentioned formula (2d) by the following formula (8), for example, phenyl GURINIYA, 4-tert-butoxy phenyl GURINIYA, 4-dimethylamino phenyl GURINIYA, etc. react.

[0043]

[Formula 9]

(The inside R1, R3, Y, X, m, and n of the above-mentioned formula is the same as that of the above respectively.)

[0044] In addition, when what has a tert-butoxy radical is used at least for the 2nd place and 2' like a bis(2, 4-G tert-butoxy phenyl) sulfoxide as a sulfoxide of the above-mentioned formula (2), the purpose compound cannot be obtained because of a solid trauma. It is also the same as when what has a tetrahydropyranyloxy radical at least in the 2nd place and 2' is used.

[0045] Moreover, in the synthesis method of the sulfonium salt by the reaction of the phenol or anisole which is the conventional technique, and a thionyl chloride, or a

sulfoxide compound, it may differ from an alt.substitution product and the Para substitution product with the reagent used since there is an active site of a phenol with the ortho position and the two para positions, and especially a meta-substitution product cannot be obtained. Furthermore, since hydrogen chloride gas occurs in the system of reaction at this reaction, it is difficult to compound a compound with an acid unstable radical like tert-butoxy benzene in a raw material. On the other hand, by the approach of this invention, since only a meta-substitution product is obtained quantitatively, the GURINIYA reagent is used and the mineral salt of a magnesium chloride etc. only generates instead of being hydrogen chloride gas, decomposition of an acid unstable radical does not advance.

[0046] In addition, although the 3-tert-butoxy phenyl GURINIYA reagent was used for the raw material of a sulfoxide and sulfonium salt in the above-mentioned synthesis method, even if it uses the GURINIYA reagent which was made to react with metal magnesium and was prepared, the sulfonium salt of the above-mentioned formula (1) is compoundable [the hydroxyl group of 3-halogenation phenol is protected by the protective group from which it can be desorbed with inactive and an acid, for example, a tetrahydropyranyl group, to a GURINIYA reagent, and].

[0047] Especially in the above-mentioned reaction, it is desirable it to be suitable to mix 1-5 mols of trialkylsilyl sulfonate of the above-mentioned formula (3) at a rate of 2-3 mols, and to add especially 1-5 mols of GURINIYA reagents of the above-mentioned formula (4) or the above-mentioned formula (8) at a rate of 2-3 mols to the sulfoxide of the above-mentioned formula (2) to the sulfoxide of the above-mentioned formula (2). Furthermore, as for these reactions, it is desirable under existence of organic bases, such as triethylamine and a pyridine, to carry out in organic solvents, such as THF and a methylene chloride, in order to prevent the desorption of the tert-butoxy radical by the acid impurity of the minute amount which exists in the trialkylsilyl sulfonate of the above-mentioned formula (3). In addition, although especially the reaction condition of these reactions is not restricted, it is desirable to consider as the reaction temperature of 0-10 degrees C.

[0048] Furthermore, in this invention, the new sulfonium salt shown by the following general formula (1) which has the acid unstable radical made into the purpose in the 3rd place of a phenyl group can be obtained by carrying out deprotection of the tert-butoxy radical of the sulfonium salt of the above-mentioned formula (1a) with an acid, and permuting the hydrogen atom of a phenolic hydroxyl group with a conventional method by acid unstable radicals, such as a tert-butoxycarbonyl radical, a tert-butoxy carbonylmethyl radical, a trialkylsilyl group, a tetrahydropyranyl group, and a methoxymethyl radical.

[0049]

[Formula 10]

(However, the inside R1, R2, Y, n, and m of the above-mentioned formula is the same as that of the above respectively.)

[0050] Thus, the new sulfonium salt of the above-mentioned formula (1) of this invention obtained It is what is suitably used as an acid generator of a chemistry magnification positive-resist ingredient. Although the sulfonium salt of this formula (1) can be blended as an acid generator and can be prepared as a chemistry magnification positive-resist ingredient of binary system (an organic solvent, alkali fusibility resin, acid generator) or three-component system (an organic solvent, alkali fusibility resin, an acid generator, lysis inhibition agent) It is suitable to prepare as a chemistry magnification positive-resist ingredient of three-component system especially.

[0051] in this case, if it is desirable that it takes the 0.5 to 15 section (the weight section and the following -- the same) for the 2 - 8 section and it does not fulfill the 0.5 sections to the alkali fusibility resin 100 weight section, there are few acid yields at the time of exposure, sensibility and resolving power may be inferior, if the 15 sections are exceeded, the permeability of a resist may fall, and especially the loadings of the sulfonium salt of the above-mentioned formula (1) as an acid generator may be inferior in resolving power

[0052] In addition, although the operation of the resist ingredient with which the sulfonium salt of the above-mentioned formula (1) was blended, optical operation, etc. can adopt a well-known lithography technique and can perform it, especially its above-mentioned resist ingredient is the optimal to detailed patterning by 254-193nm far-ultraviolet light and the electron ray.

[0053]

EXAMPLE

[Example] Although an example and the example of a comparison, and the example of combination are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example. In addition, each section in each example is the weight section.

[0055] [Example 1]

Synthetic bis(3-tert-butoxy phenyl) sulfoxide 17.8g (0.052 mols) of trifluoromethansulfonic acid tris (3-tert-butoxy phenyl) sulfonium was dissolved in THF52g, and it cooled in the iced water bath. The reaction was riped for 30 minutes, triethylamine 5.3g (0.052 mols) having been added to this, and having been dropped,

controlling trimethylsilyl trifluoromethane sulfonate 28.6g (0.13 mols) not to exceed 10 degrees C, and having used reaction temperature as 0-10 degrees C. It was dropped controlling the GURINIYA reagent which used 3-tert-butoxy chlorobenzene 24.0g (0.13 mols), metal magnesium 3.2g (0.13 mols), and THF 40g for this solution, and was prepared with the conventional method not to exceed 10 degrees C. Furthermore, the reaction was riped for 30 minutes, having used reaction temperature as 0-10 degrees C. After adding 300g of ammonium-chloride water solutions to reaction mixture 20% and performing a halt and liquid separation of a reaction, chloroform 300g was added to the organic layer. After rinsing an organic layer twice using 200g of water, reduced pressure distilling off of the solvent was carried out, and oily matter was obtained. When this oily matter was applied to the column chromatography (silica gel: an extract, chloroform-methanol), trifluoro methansulfonic acid tris (3-tert-butoxy phenyl) sulfonium of the yield of 10.5g (29% of yield) and 99% of purity was isolated.

[0056] The result of the nuclear-magnetic-resonance spectrum (NMR) of the obtained trifluoro methansulfonic acid tris (3-tert-butoxy phenyl) sulfonium, an infrared spectrum (IR), an elemental-analysis value, and an ultraviolet absorption spectrum (UV) is shown below. In addition, the value of the ultraviolet absorption spectrum of trifluoro methansulfonic acid triphenylsulfonium and trifluoro methansulfonic acid tris (4-tert-butoxy phenyl) sulfonium is also shown as an example of a comparison.

[0057]

[Formula 11]

(a) 1.25 Singlet 27H(b)7.05-7.06 Triplet 3H(c) (e)7.25-7.29 Multiplet 6H(d)7.51-7.57 Triplet 3HIR:(cm⁻¹) 2980, 1587, 1564, 1477, 1423, 1394, 1369, 1263, 1259, 1159, 1031, 933, 912, 638

Elemental-analysis value: (%) C₃₁H₃₉O₆S₂F₃ theoretical value C:59.2 H:6.2 analysis value C:59.1 H:6.1 [0058]

[Table 1]

[0059] [Example 2] Except using phenyl GURINIYA instead of 3-tert-butoxy phenyl GURINIYA of an example 1, when reacted like the example 1, trifluoro methansulfonic acid bis(3-tert-butoxy phenyl) phenyl sulfonium was obtained at 98% of purity, and 35% of yield.

[0060] [Example 3] Except using a diphenyl sulfoxide instead of the sulfoxide of an example 1, when reacted like the example 1, trifluoro methansulfonic acid (3-tert-butoxy phenyl) diphenyl sulfonium was obtained at 98% of purity, and 27% of yield.

[0061] [Example 4] Except using a bis(4-dimethylamino phenyl) sulfoxide instead of the sulfoxide of an example 1, when reacted like the example 1, trifluoro methansulfonic

acid (3-tert-butoxy phenyl) bis(4-dimethylamino phenyl) sulfonium was obtained at 98% of purity, and 27% of yield.

[0062] [Example 5] Except using 4-dimethylamino phenyl GURINIYA instead of the GURINIYA reagent of an example 1, when reacted like the example 1, trifluoromethanesulfonic acid bis(3-tert-butoxy phenyl) (4-dimethylamino phenyl) sulfonium was obtained at 98% of purity, and 33% of yield.

[0063] [Examples 6-10]. ***** made to react like examples 1-5 and the sulfonium salt which has p-toluenesulfonic acid in the respectively following counter anions were obtained except using the trimethylsilyl-p-toluene sulfonate (113-117 degrees C of boiling points, 0.5 - 0.6mmHg) obtained by making p-toluenesulfonic acid and trimethylsilyl chloride react with a conventional method instead of the trimethylsilyl trifluoromethane sulfonate used in the examples 1-5.

Example 6: p-toluenesulfonic-acid tris (3-tert-butoxy phenyl) sulfonium 99% of purity 35% example 7 of yield: p-toluenesulfonic-acid bis(3-tert-butoxy phenyl) phenyl sulfonium 99% of purity 28% Example 8 of Yield: p-toluenesulfonic-acid (3-tert-butoxy phenyl) diphenyl sulfonium 99% of purity 25% example 9 of yield: p-toluenesulfonic-acid (3-tert-butoxy phenyl) bis(4-dimethylamino phenyl) sulfonium 97% of purity The 31% example 10 of yield: P-toluenesulfonic-acid bis(3-tert-butoxy phenyl) (4-dimethylamino phenyl) sulfonium 98% of purity 32% [0064] of yield [Examples 11-15] ***** made to react like examples 1-5 and the sulfonium salt which has a nonafluorobutane sulfonic acid in the respectively following counter anions were obtained except using the trimethylsilyl nonafluorobutane sulfonate obtained by making a nonafluorobutane sulfonic acid and trimethylsilyl chloride react with a conventional method instead of the trimethylsilyl trifluoromethane sulfonate used in the examples 1-5.

Example 11: nonafluorobutane sulfonic-acid tris (3-tert-butoxy phenyl) sulfonium 99% of purity 31% example 12 of yield: nonafluorobutane sulfonic-acid bis(3-tert-butoxy phenyl) phenyl sulfonium 99% of purity The 28% example 13 of yield : A nonafluorobutane sulfonic acid (3-tert-butoxy phenyl) diphenyl sulfonium 99% of purity The 18% example 14 of yield : A nonafluorobutane sulfonic acid (3-tert-butoxy phenyl) bis(4-dimethylamino phenyl) sulfonium 98% of purity 27% example 15 of yield: nonafluorobutane sulfonic-acid bis(3-tert-butoxy phenyl) (4-dimethylamino phenyl) sulfonium 97% of purity 25% [0065] of yield [Examples 16-19] Deprotection of the new sulfonium salt which has the tert-butoxy radical obtained in the examples 1-15 in the 3rd place is carried out in a methanol or ethanol using the same sulfonic acid as a counter anion (for example, trifluoromethane sulfonate and p-toluene sulfonate). After obtaining corresponding 3-hydroxyphenyl sulfonium salt almost quantitatively, The sulfonium salt which has an acid unstable radical as shown below

by using G tert-butyl-JIKARUBONETO or chloroacetic-acid-tert-butyl, and a dihydropyran with a conventional method in the 3rd place of a phenyl group was compounded.

Example 16: NONARI fluoro butane sulfonic-acid bis(3-tert-butoxycarbonyloxy phenyl) phenyl sulfonium 98% of purity, The 23% example 17 of yield: Trifluoro methansulfonic acid (3-tert-butoxycarbonyl methyloxy phenyl) diphenyl sulfonium 98% of purity, The 25% example 18 of yield: P-toluenesulfonic-acid (3-tert-butoxycarbonyloxy phenyl) diphenyl sulfonium 98% of purity, The 19% example 19 of yield: Nonafluorobutane sulfonic-acid tris (3-tert-butoxycarbonyl methyloxy phenyl) sulfonium 98% of purity, 18% [0066] of yield The molar extinction coefficient of an ultraviolet absorption spectrum [in / the 4th place / as a substitution product (3-tert-butoxy phenyl sulfonium salt) and an example of a comparison / the 3rd place / 248nm of a substitution product (4-tert-butoxy phenyl sulfonium salt)] of the new sulfonium salt of the above-mentioned examples 1-10 is shown in Table 2.

[0067] It turned out that the effectiveness shows up most greatly in tris (tert-butoxy phenyl) sulfonium salt with many tert-butoxy phenyl groups by the ability lessening 248nm light absorption when the sulfonium salt of this invention is not the 4th place and has a tert-butoxy radical in the 3rd place so that clearly from the result of Table 2.

[0068]

[Table 2]

[0069] [The examples 1-14 of combination and examples 1-5 of comparison combination] Polyhydroxy styrene which is shown by the following formula (Polym.1) as shown in Tables 3 and 4 and which protected the hydrogen atom of a hydroxyl group by the tert-BUTOSHIKI carbonyl group partially, The polyhydroxy styrene which is shown by the polyhydroxy styrene or the following type (Polym.3) which is shown by the following formula (Polym.2), and which protected the hydrogen atom of a hydroxyl group by tert-butyl partially and which protected the hydrogen atom of a hydroxyl group by the tetrahydropyranyl group partially, The acid generator chosen from the onium salt shown by (PAG.5) from the following type (PAG.1), The lysis inhibition agent of the 2 and 2'-bis(4-tert-butoxycarbonyloxy phenyl) propane shown by the following formula (Data Resources.1) was dissolved in 1-ethoxy-2-propanol, and the resist constituent of the various presentations shown in Table 3 was prepared.

[0070] After preparing resist liquid by filtering the obtained resist constituent with the 0.2-micrometer filter made from Teflon, spin coating of this resist liquid was carried out to up to the silicone wafer, and it applied to 0.8 micrometers.

[0071] Subsequently, BEKU [this silicone wafer / with the 100-degree C hot plate] for 120 seconds. Furthermore, when it exposed using the excimer laser stepper (NIKON

CORP., NSR2005EXNA=0.5), BEKU during 60 seconds was given at 90 degrees C and negatives were developed in the water solution of 2.38% of tetramethylammonium hydroxide, the pattern of a positive type was able to be obtained.

[0072] The obtained resist pattern was evaluated as follows. A result is shown in Tables 3 and 4.

The resist-pattern evaluation approach: It asked for sensibility (Eth) first. Next, minimum line width of separated Rhine in this light exposure and a tooth space was made into the resolution of an evaluation resist by making into the optimal light exposure (sensibility: Eop) light exposure which resolves the top and the bottom of a 0.35-micrometer Rhine and a tooth space by 1:1. Moreover, the configuration of the resolved resist pattern was observed using the scanning electron microscope.

[0073]

[Formula 12]

[0074]

[Formula 13]

[0075]

[Table 3]

[0076]

[Table 4]

[0077] [the examples 15-28 of combination, and the examples 5-8 of comparison combination] -- it is shown in Tables 5 and 6 -- as -- as an acid generator -- the following (PAG.6-8) -- or -- having mentioned above (PAG 4 and 5) -- the positive type pattern was obtained like the above-mentioned example 1 of combination except using. In addition, the nitrogen content compound for PED stability was added to the example 28 of combination as an additive.

[0078] The obtained resist pattern was similarly estimated as the above. Furthermore, the PED stability of a resist changed after exposure and neglect time amount with the optimal light exposure, performed PEB, and the time amount by which change of a resist pattern configuration was observed, for example, the Rhine pattern, became T-top, and it evaluated it by time amount it became impossible to resolve. It is rich in PED stability, so that this time amount is long. The above result is shown in Tables 5 and 6.

[0079]

[Formula 14]

[0080]

[Table 5]

[0081]

[Table 6]

[Translation done.]

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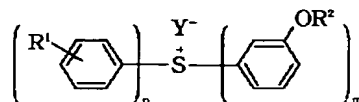
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(54) 【発明の名称】 スルホニウム塩

(57) 【要約】

【目的】 微細加工技術に適した高解像度を有し、化学増幅ポジ型レジスト材料の成分として好適な成分を開発する。



(但し、式中R¹は水素原子、アルキル基、アルコキシ基又はジアルキルアミノ基であり、OR²は酸不安定基であり、Yは置換又は非置換のアルキルスルホネート又

【構成】 下記一般式(1)で示され、分子中のフェニル基の3位に少なくとも1つの酸不安定基を有することを特徴とするスルホニウム塩。

【化1】

... (1)

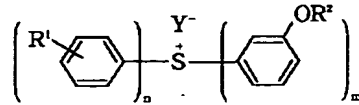
はアリールスルホネートである。nは0~2の整数、mは1~3の整数で、かつnとmの和は3である。)

1

2

【特許請求の範囲】

【請求項1】 下記一般式(1)で示され、分子中のフェニル基の3位に少なくとも1つの酸不安定基を有する



(但し、式中R¹は水素原子、アルキル基、アルコキシ基又はジアルキルアミノ基であり、OR²は酸不安定基であり、Yは置換又は非置換のアルキルスルホネート又はアリールスルホネートである。nは0～2の整数、mは1～3の整数で、かつnとmの和は3である。)

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、微細加工技術に適した化学増幅ポジ型レジスト材料の成分として好適な新規なスルホニウム塩に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】 LSIの高集積化と高速度化に伴い、パターンルールの微細化が求められている中、次世代の微細加工技術として遠紫外線リソグラフィーが有望視されている。遠紫外線リソグラフィーは、0.3～0.4μmの加工も可能であり、光吸収の低いレジスト材料を用いた場合、基板に対して垂直に近い側壁を有したパターン形成が可能とな

ことを特徴とするスルホニウム塩。

【化1】

... (1)

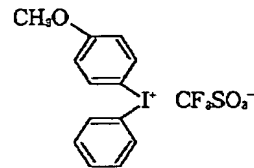
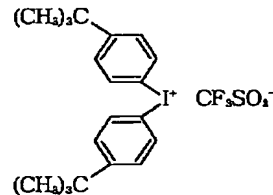
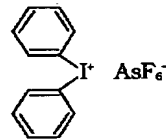
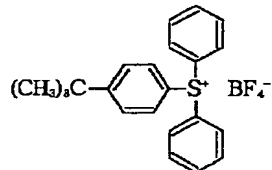
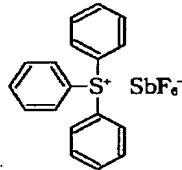
る。また、近年、遠紫外線の光源として高輝度なKrFエキシマレーザーを利用する技術が注目されており、これが量産技術として用いられるためには、光吸収が低く、高感度なレジスト材料が要望されている。

【0003】 このような観点から、近年開発された酸を触媒とした化学増幅ポジ型レジスト材料(特公平2-27660号、特開昭63-27829号公報等)は、感度、解像度、ドライエッチング耐性が高く、優れた特徴を有するもので、遠紫外線リソグラフィーに特に有望なレジスト材料である。

【0004】 この場合、化学増幅ポジ型レジスト材料においては、配合する酸発生剤が化学増幅ポジ型レジスト材料としての機能に特に大きな影響を及ぼすことが知られている。このような酸発生剤の代表的なものとしては、下記に示すオニウム塩が挙げられる。

【0005】

【化2】



【0006】 上記オニウム塩は、それ自体が油溶性の化合物であるので、レジスト成分として配合するとレジスト材料のアルカリ水溶液に対する溶解度を低下させると共に、現像時の膜減りを抑える効果を有する。

【0007】 しかしながら、ポジ型レジスト材料の場合、酸発生剤が高エネルギー線を吸収することにより生成する分解生成物もやはり油溶性であることから、この

分解生成物が露光部のアルカリ水溶液に対する溶解速度を低下させ、露光部と未露光部のアルカリ溶解速度比(溶解コントラストという)を大きくすることができない。このため、上記オニウム塩を用いた化学増幅ポジ型レジスト材料は、アルカリ現像に際して解像性が低く、露光部の抜け性が悪いため、パターン形状が矩形にはならず、台形状の順テーパーとなるという欠点があった。

【0008】そこで、この問題を解決するため、酸不安定基であるtert-ブトキシ基をトリフェニルスルホニウム塩のp位に導入し、高エネルギー線照射により分解、生成する酸の作用でアルカリ溶解性を持つフェノール誘導体を生成させ、溶解コントラストを大きくすることが行われている(特願平6-317626号参照)。しかし、このようなフェノール誘導体を生じるスルホニウム塩を用いても反射率の低い基板上で露光を行った場合には解像度の点で満足するものを得ることは困難であった。

【0009】これは、上記スルホニウム塩の250nm付近の透過率が低く、レジスト膜としての透過性を低下させるため、反射率の低い基板を用いて露光を行った場合にレジスト膜上部、下部での光強度が異なり、酸の発生量に差が現れ、解像性を低下させるためと考えられる。

【0010】また、従来の化学増幅ポジ型レジスト材料は、遠紫外線、電子線、X線リソグラフィーを行った際、露光からPEB(Post Exposure Bake)までの放置時間が長くなると、パターン形成した際にラインパターンがT-トップ形状になる、即ちパターン上部が太くなるという問題[PED(Post Exposure Deley)と呼ぶ]があり、これはレジスト膜表面の溶解性が低下するためと考えられ、実用に供する場合の大きな欠点となっている。この欠点のため、従来の化学増幅ポジ型レジスト材料は、リソグラフィー工程での寸法制御を難しくし、ドライエッチングを用いた基板加工に際しても寸法制御を損ねるという問題がある[参考:W. Hinsberg, et. al., J. Photopolym. Sci. Technol., 6(4), 535-546(1993), T. Kumada, et. al., J. Photopolym. Sci. Technol., 6(4), 571-574(1993)]。この問題を解決し、満足できる化学増幅ポジ型レジスト材料は未だない。

【0011】化学増幅ポジ型レジスト材料において、PEDの問題の原因は、空気中の塩基性化合物が大きく関与していると考えられている。露光により発生したレジスト膜表面の酸は空気中の塩基性化合物と反応、失活し、PEDまでの放置時間が長くなればそれだけ失活する酸の量が増加するため、酸不安定基の分解が起こり難くなる。そのため、表面に難溶化層が形成され、パターンがT-トップ形状となるのである。

【0012】なお、この場合は塩基性化合物を添加することにより、空気中の塩基性化合物の影響を抑えることができるため、PEDにも効果があることが知られている(特開平5-232706号、同5-249683号公報等)が、本発明者の検討によると、ここで用いられる塩基性化合物は、揮発によりレジスト膜中に取り込まれなかったり、レジスト材料の各成分との相溶性が悪く、レジスト膜中での分散が不均一であるために効果の再現性に問題があり、しかも解像性を落としてしまうことがわかった。

【0013】従って、上記問題のない高性能の化学増幅ポジ型レジスト材料を与える新規な成分の開発が望まれる。

【0014】本発明は上記事情に鑑みなされたもので、微細加工技術に適した高解像性を有する化学増幅ポジ型レジスト材料の成分として好適な新規なスルホニウム塩を提供することを目的とする。

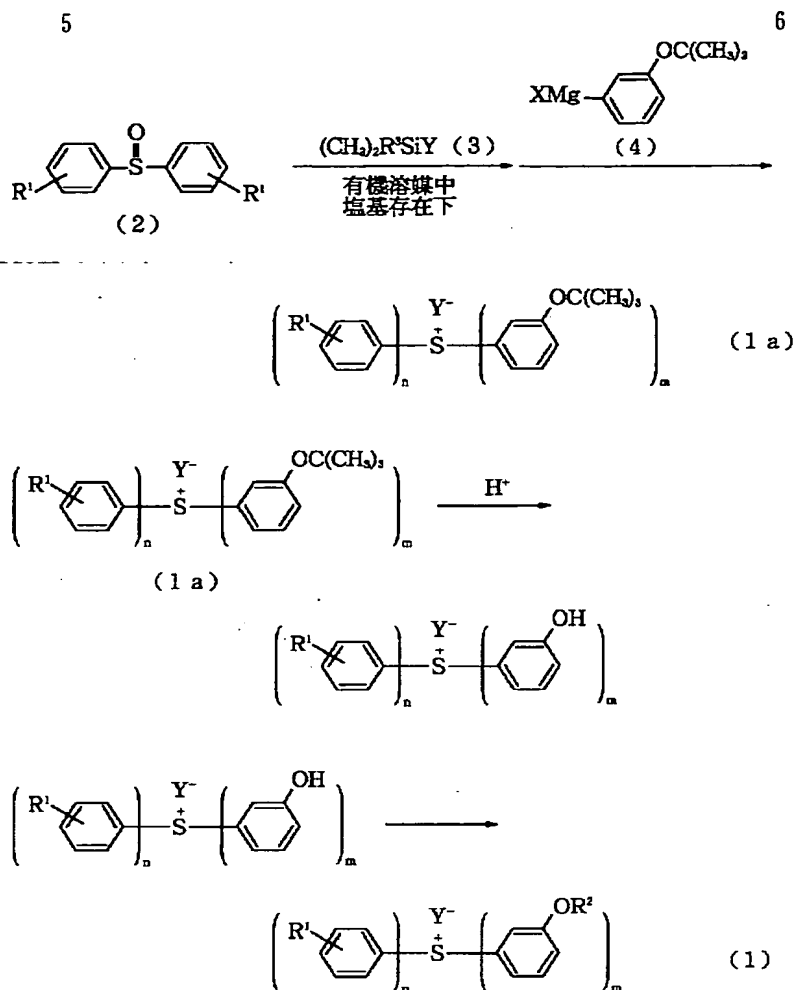
【0015】

【課題を解決するための手段及び作用】本発明者は上記目的を達成するため鋭意検討を重ねた結果、下記反応式のように下記一般式(2)で示されるジアリールスルホキシドと下記一般式(3)で示されるトリアルキルシリルスルホネートとを反応させ、更に3-tert-ブトキシフェニルクロリドと金属マグネシウムとの反応で調製し得る下記一般式(4)で示されるグリニヤ試薬を反応させることにより、下記一般式(1a)で示されるフェニル基の3位にtert-ブトキシ基を有する新規なスルホニウム塩が得られることを見出した。更に、この下記一般式(1a)で示されるスルホニウム塩のtert-ブトキシ基を酸により脱保護し、常法によりtert-ブトキシカルボニル基、tert-ブトキシカルボニルメチル基、トリアルキルシリル基、テトラヒドロピラニル基、メトキシメチル基等からなる酸不安定基をフェニル基の3位に置換させることにより、フェニル基の3位に少なくとも1つの酸不安定基を持つ下記式

(1)の新規なスルホニウム塩が得られ、かかる上記式(1)のスルホニウム塩が微細加工技術に適した高解像性を有する化学増幅ポジ型レジスト材料の成分として好適で、特に遠紫外線リソグラフィーにおいて大いに威力を発揮し得ることを見出した。

【0016】

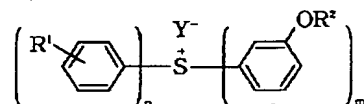
【化3】



(但し、式中 R^1 は水素原子、アルキル基、アルコキシ基又はジアルキルアミノ基、 OR^2 は酸不安定基であり、 R^3 はメチル基又はtert-ブチル基である。Yは置換又は非置換のアルキルスルホネート又はアリールスルホネートである。nは0~2の整数、mは1~3の整数で、かつnとmの和は3である。)

【0017】即ち、本発明の上記式(1)のスルホニウム塩は、化合物自体のアルカリ溶解性は低いものの、高エネルギー線照射による分解によって生成する酸、レジスト材料中の水分及びPEB(Post Exposure Bake)の作用で、効率良く酸不安定基が分解し、アルカリ溶解性の高いフェノール部位又はtert-ブトキシカルボニルメチルオキシ基のような三級カルボン酸エステル基を有する場合はカルボン酸部位が生成するため、より大きな溶解コントラストを得ることができる。

【0018】従って、上記式(1)のスルホニウム塩



(但し、式中 R^1 は水素原子、アルキル基、アルコキシ

30 基又はジアルキルアミノ基であり、 OR^2 は酸不安定基は、化学増幅ポジ型レジスト材料の酸発生剤として優れた性能を発揮することができ、上記式(1)のスルホニウム塩を含有するレジスト材料は、上記式(1)のスルホニウム塩の酸不安定基の効果により、大きな溶解コントラストを有し、特に250nm付近の光源を用いた場合には、酸素原子が硫黄原子と共鳴構造を取り得ない3位に置換されていることにより250nm付近の透過率を無置換のものと同程度以上に高めることが可能で、それ故、高解像度、広範囲の焦点深度を有するレジスト像を得ることができるものである。

【0019】即ち、本発明は、(A)下記一般式(1)で示され、分子中のフェニル基の3位に少なくとも1つの酸不安定基を有することを特徴とするスルホニウム塩を提供する。

【0020】

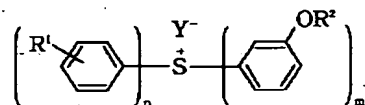
【化4】

... (1)

50 基又はジアルキルアミノ基であり、 OR^2 は酸不安定基

であり、Yは置換又は非置換のアルキルスルホネート又はアリールスルホネートである。nは0～2の整数、mは1～3の整数で、かつnとmの和は3である。）

【0021】以下、本発明につき更に詳細に説明すると、本発明の新規なスルホニウム塩は、下記一般式



(但し、式中R¹は水素原子、アルキル基、アルコキシ基又はジアルキルアミノ基であり、OR²は酸不安定基であり、Yは置換又は非置換のアルキルスルホネート又はアリールスルホネートである。nは0～2の整数、mは1～3の整数で、かつnとmの和は3である。)

【0023】上記式(1)において、R¹は水素原子、アルキル基、アルコキシ基又はジアルキルアミノ基であり、具体的にアルキル基としては、メチル基、エチル基、プロピル基、イソプロピル基、n-ブチル基、sec-ブチル基、tert-ブチル基、ヘキシル基、シクロヘキシル基等の炭素数1～8のものが好適であり、中でもメチル基、エチル基、イソプロピル基、tert-ブチル基がより好ましく用いられる。アルコキシ基としては、メトキシ基、エトキシ基、プロポキシ基、イソプロポキシ基、n-ブトキシ基、sec-ブトキシ基、tert-ブトキシ基、ヘキシロキシ基、シクロヘキシロキシ基等の炭素数1～8のものが好適であり、中でもメトキシ基、エトキシ基、イソプロポキシ基、tert-ブトキシ基がより好ましく用いられる。ジアルキルアミノ基としては、ジメチルアミノ基、ジエチルアミノ基、ジプロピルアミノ基等の炭素数1～4のアルキル基を有するアミノ基が用いられるが、中でもジメチルアミノ基が望ましい。

【0024】OR²は酸不安定基である。ここで、酸不安定基としては、例えばtert-ブトキシ基等の三級アルコキシ基、tert-ブトキシカルボニルオキシ基等の炭酸エステル基、tert-ブトキシカルボニルメチルオキシ基等の三級カルボン酸エステル基、トリメチルシリルオキシ基、トリエチルシリルオキシ基、tert-ブチルジメチルシリルオキシ基等のトリアルキルシリルオキシ基、テトラヒドロピラニルオキシ基、メトキシメチルオキシ基、エトキシエチルオキシ基等のアセタール又はケタール基などが挙げられる。

【0025】また、Yは置換又は非置換のアルキルスルホネート又はアリールスルホネートであり、例えばトリフルオロメタンスルホネート、ノナフルオロブタンスルホネート、p-トルエンスルホネートが好適である。nは0～2の整数、mは1～3の整数で、かつnとmの和は3である。

【0026】なお、本発明では、特にカウンターアニオン(Y⁻)にp-トルエンスルホン酸アニオン(p-ト

(1)で示され、分子中のフェニル基の3位に少なくとも1つの酸不安定基を有するものである。

【0022】

【化5】

ルエンスルホネート)を持つスルホニウム塩をレジスト材料の成分として用いると、そのp-トルエンスルホン酸アニオンの効果、即ちレジスト膜表面での空気中の塩基性化合物による酸の失活の影響を非常に小さいものとすることができるため、表面難溶層の形成を抑えることができ、PED安定性が良好で、T-トップ形状の原因である表面難溶層の問題、即ちPEDの問題を充分に解決し得、より良好な感度を得ることができる。

【0027】このような上記式(1)のスルホニウム塩としては、具体的に下記のもの为例示される。即ち、酸不安定基としてtert-ブトキシ基を有するスルホニウム塩としては、例えばトリフルオロメタンスルホン酸(3-tert-ブトキシフェニル)ジフェニルスルホニウム、p-トルエンスルホン酸(3-tert-ブトキシフェニル)ジフェニルスルホニウム、ノナフルオロブタンスルホン酸(3-tert-ブトキシフェニル)ジフェニルスルホニウム、トリフルオロメタンスルホン酸ビス(3-tert-ブトキシフェニル)フェニルスルホニウム、p-トルエンスルホン酸ビス(3-tert-ブトキシフェニル)フェニルスルホニウム、ノナフルオロブタンスルホン酸ビス(3-tert-ブトキシフェニル)フェニルスルホニウム、トリフルオロメタンスルホン酸トリス(3-tert-ブトキシフェニル)スルホニウム、p-トルエンスルホン酸トリス(3-tert-ブトキシフェニル)スルホニウム、ノナフルオロブタンスルホン酸トリス(3-tert-ブトキシフェニル)スルホニウム、トリフルオロメタンスルホン酸(3-tert-ブトキシフェニル)ビス(4-ジメチルアミノフェニル)スルホニウム、p-トルエンスルホン酸(3-tert-ブトキシフェニル)ビス(4-ジメチルアミノフェニル)スルホニウム、ノナフルオロブタンスルホン酸(3-tert-ブトキシフェニル)ビス(4-ジメチルアミノフェニル)スルホニウム、トリフルオロメタンスルホン酸ビス(3-tert-ブトキシフェニル)(4-ジメチルアミノフェニル)スルホニウム、p-トルエンスルホン酸ビス(3-tert-ブトキシフェニル)(4-ジメチルアミノフェニル)スルホニウム、ノナフルオロブタンスルホン酸ビス(3-tert-ブトキシフェニル)(4-ジメチルアミノフェニル)スルホニウムなどが挙げられる。

【0028】酸不安定基としてtert-ブトキシカル

ボニルオキシ基を持つスルホニウム塩としては、トリフルオロメタンスルホン酸ビス(3-tert-ブトキシカルボニルオキシフェニル)フェニルスルホニウム、p-トルエンスルホン酸ビス(3-tert-ブトキシカルボニルオキシフェニル)フェニルスルホニウム、トリフルオロメタンスルホン酸トリス(3-tert-ブトキシカルボニルオキシフェニル)スルホニウム、p-トルエンスルホン酸トリス(3-tert-ブトキシカルボニルオキシフェニル)スルホニウム、ノナフルオロブタン

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タンスルホン酸トリス(3-tert-ブトキシカルボニルオキシフェニル)スルホニウム、トリフルオロメタンスルホン酸ビス(3-tert-ブトキシカルボニルオキシフェニル)フェニルスルホニウム、p-トルエンスルホン酸ビス(3-tert-ブトキシカルボニルオキシフェニル)フェニルスルホニウム、トリフルオロメタンスルホン酸トリス(3-tert-ブトキシカルボニルメチルオキシフェニル)フェニルスルホニウム、p-トルエンスルホン酸ビス(3-tert-ブトキシカルボニルメチルオキシフェニル)フェニルスルホニウム、トリフルオロメタンスルホン酸トリス(3-tert-ブトキシカルボニルメチルオキシフェニル)スルホニウム、ノナフルオロブタン

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【0029】酸不安定基としてtert-ブトキシカルボニルメチルオキシ基を持つスルホニウム塩としては、トリフルオロメタンスルホン酸ビス(3-tert-ブトキシカルボニルメチルオキシフェニル)フェニルスルホニウム、p-トルエンスルホン酸ビス(3-tert-ブトキシカルボニルメチルオキシフェニル)フェニルスルホニウム、トリフルオロメタンスルホン酸トリス(3-tert-ブトキシカルボニルメチルオキシフェニル)フェニルスルホニウム、トリフルオロメタンスルホン酸トリス(3-tert-ブトキシカルボニルメチルオキシフェニル)スルホニウム、ノナフルオロブタン

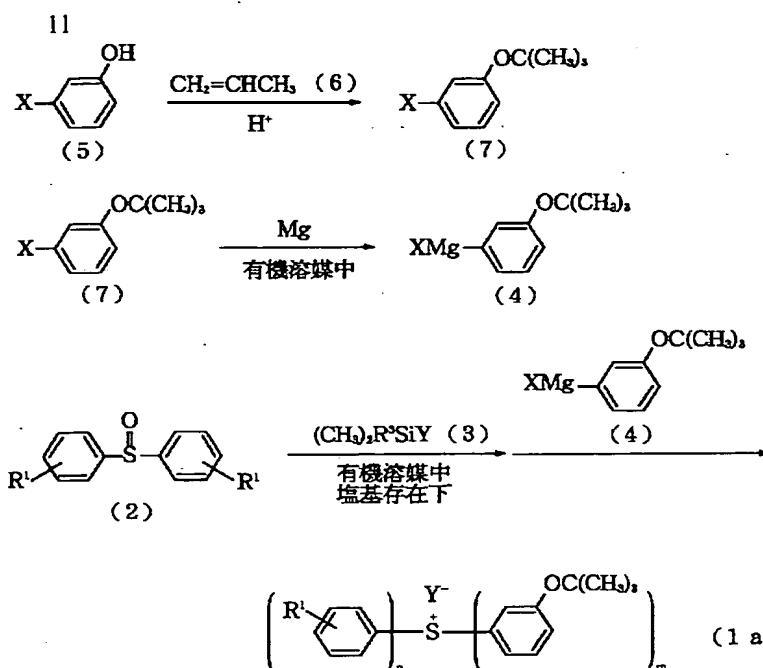
キシフェニル)スルホニウム、トリフルオロメタンスルホン酸(3-(2-テトラヒドロピラニル)-オキシフェニル)ビス(4-ジメチルアミノフェニル)スルホニウム、p-トルエンスルホン酸ビス(3-(2-テトラヒドロピラニル)-オキシフェニル)(4-ジメチルアミノフェニル)スルホニウムなどが挙げられ、メトキシメチル基を持つものとして、トリフルオロメタンスルホン酸ビス(3-メトキシメチルオキシフェニル)フェニルスルホニウム、トリフルオロメタンスルホン酸トリス(3-メトキシメチルオキシフェニル)スルホニウム、ノナフルオロブタンスルホン酸トリス(3-メトキシメチルオキシフェニル)スルホニウム、トリフルオロメタンスルホン酸(3-メトキシメチルオキシフェニル)ビス(4-ジメチルアミノフェニル)スルホニウム、p-トルエンスルホン酸ビス(3-メトキシメチルオキシフェニル)(4-ジメチルアミノフェニル)スルホニウムなどが挙げられる。

【0031】酸不安定基としてトリアルキルシリルオキシ基を持つスルホニウム塩としては、トリフルオロメタンスルホン酸ビス(3-トリメチルシリルオキシフェニル)フェニルスルホニウム、p-トルエンスルホン酸ビス(3-トリエチルシリルオキシフェニル)フェニルスルホニウム、トリフルオロメタンスルホン酸トリス(3-トリメチルシリルオキシフェニル)スルホニウム、ノナフルオロブタンスルホン酸トリス(3-トリメチルシリルオキシフェニル)スルホニウム、トリフルオロメタンスルホン酸(3-トリエチルシリルオキシフェニル)ビス(4-ジメチルアミノフェニル)スルホニウム、p-トルエンスルホン酸ビス(3-トリメチルシリルオキシフェニル)(4-ジメチルアミノフェニル)スルホニウムなどが挙げられる。

【0032】本発明の上記式(1)のスルホニウム塩は、以下のような経路により合成することができる。即ち、例えばまず下記一般式(5)で示される3-ハロゲン化フェノールと下記一般式(6)で示されるイソブテンとを酸により縮合させて得られる下記一般式(7)で示される3-ハロゲン化tert-ブトキシベンゼンを常法によりTHF中金属マグネシウムと反応させ、下記一般式(4)で示される3-tert-ブトキシフェニルグリニヤ(グリニヤ試薬)とする。次に、有機溶媒中で下記一般式(2)で示されるスルホキシドに下記一般式(3)で示されるトリアルキルシリルスルホネートを反応させ、更に下記式(4)のグリニヤ試薬を反応させることにより、下記一般式(1a)で示される酸不安定基として3-tert-ブトキシフェニル基を持つスルホニウム塩を合成することができる。

【0033】

【化6】



(但し、式中 R^1 、 R^2 、 R^3 、 Y 、 m 、 n はそれぞれ上記と同様であり、 X は臭素原子又は塩素原子である。)

【0034】上記反応において、上記式(5)の3-ハロゲン化フェノールと上記式(6)のイソブテンの反応は、「実験化学講座第四版、有機合成2、p200、日本化学会編、丸善」や「J. Holcombe and

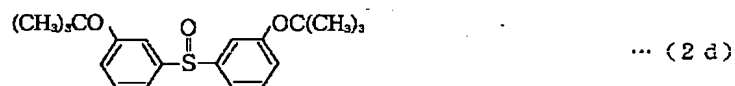
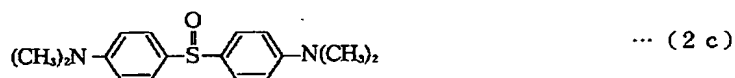
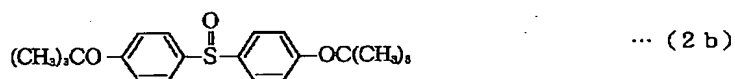
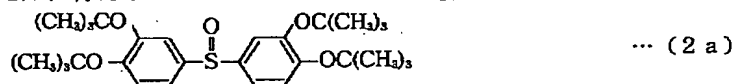
T. Livinghouse J. Org. Chem., 111~115, 51. (1986)」に準じて行うことができる。この場合、上記式(5)の3-ハロゲン化フェノールと上記式(6)のイソブテンとを反応させる際、式(6)のイソブテンを式(5)の3-ハロゲン化フェノールに対して1~10モル、特に3~5モルの割合で加え、トリフルオロメタンスルホン酸等の強酸を触媒として式(5)の3-ハロゲン化フェノールに対して0.01~0.1モル、特に0.01~0.05

モルの割合で添加するのが好ましい。また、反応は塩化メチレン等の有機溶媒中で $-40 \sim -70^\circ\text{C}$ の温度範囲で0.5~4時間行うことが望ましい。

【0035】また、上記式(2)のスルホキシドとしては、ジフェニルスルホキシド、下記式(2a)で示されるビス(3,4-ジ-tert-ブトキシフェニル)スルホキシド、下記式(2b)で示されるビス(4-tert-ブトキシフェニル)スルホキシド、下記式(2c)で示されるビス(4-ジメチルアミノフェニル)スルホキシド、上記式(4)のグリニヤ試薬と塩化チオニルの縮合生成物である下記式(2d)で示されるビス(3-tert-ブトキシフェニル)スルホキシド等を用いることが望ましい。

【0036】

【化7】



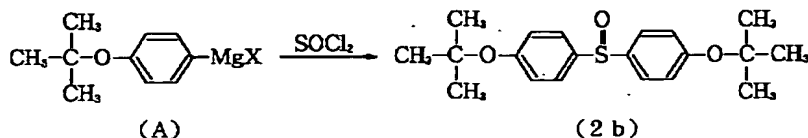
【0037】なお、これらスルホキシド化合物の合成は特願平6-26171号記載の方法に準じて行うことができる。

【0038】例えば上記式(2b)の化合物を得る場合

は、下記式(A)で示されるp-tert-ブトキシフェニルグリニヤに塩化チオニルを反応させるといった方法によって行うことができる。

【0039】

【化8】



(Xは塩素又は臭素原子を示す。)

【0040】この場合、反応は塩化メチレン、THFの有機溶剤中で行うことが好ましい。また、グリニヤ試薬に塩化チオニルを反応させる際にはグリニヤ試薬に対して塩化チオニルを1/6～1/2モル、好ましくは1/3～1/2モルの割合で滴下し、反応条件は-78℃～70℃、好ましくは-60℃～10℃であり、滴下時間は10～120分、好ましくは45～90分である。反応終了後は溶媒層を水洗、乾燥、濃縮後、再結晶あるいはカラムクロマトグラフィーにより目的化合物を得ることができる。

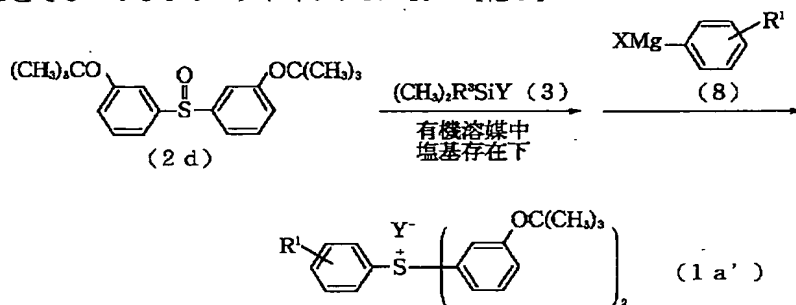
【0041】本発明では、上記式(2a)、(2b)、(2c)、あるいはジフェニルスルホキシド等のスルホキシドを原料にすることで3-tert-ブトキシフェニル

ニル基を1個持つ新規なスルホニウム塩を合成することができる。また、上記式(2d)のスルホキシドを原料に用いることにより、3-tert-ブトキシフェニル基を3個持つ新規なスルホニウム塩を合成することができる。

【0042】また、3-tert-ブトキシフェニル基を2個持つ新規なスルホニウム塩は、上記式(2d)のビス(3-tert-ブトキシフェニル)スルホキシドと、下記式(8)で示されるアリールグリニヤ試薬、例えばフェニルグリニヤ、4-tert-ブトキシフェニルグリニヤ、4-ジメチルアミノフェニルグリニヤ等とを反応させることにより合成することができる。

【0043】

【化9】



(上記式中R¹、R²、Y、X、m、nはそれぞれ上記と同様である。)

【0044】なお、上記式(2)のスルホキシドとしてビス(2,4-ジ-tert-ブトキシフェニル)スルホキシドのような2位及び2'位にtert-ブトキシ基を有するものを用いた場合は、立体傷害のため目的化合物を得ることができない。テトラヒドロピラニルオキシ基を2位及び2'位に持つものを用いた場合も同様である。

【0045】また、従来技術であるフェノール又はアニソールと塩化チオニルの反応によるスルホニウム塩又はスルホキシド化合物の合成法では、フェノールの活性部位がオルト位、パラ位と二つあるため用いる試薬によりオルト置換体、パラ置換体と異なる可能性があり、特にメタ置換体は得ることができない。更に、この反応では、反応系中に塩化水素ガスが発生するため、tert-ブトキシベンゼンのような酸不安定基を持つ化合物を原料に合成を行うことは困難である。これに対して本発明の方法では、グリニヤ試薬を用いているため定量的にメタ置換体のみが得られ、塩化水素ガスの代わりに塩化マグネシウム等の無機塩が生成するだけであるので、酸

不安定基の分解は進行しない。

【0046】なお、上記合成法においては3-tert-ブトキシフェニルグリニヤ試薬をスルホキシド及びスルホニウム塩の原料に用いたが、グリニヤ試薬に対して不活性かつ酸により脱離可能な保護基、例えばテトラヒドロピラニル基で3-ハロゲン化フェノールの水酸基を保護し、金属マグネシウムと反応させて調製したグリニヤ試薬を用いても上記式(1)のスルホニウム塩を合成することができる。

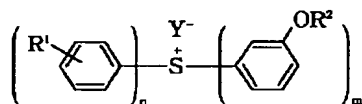
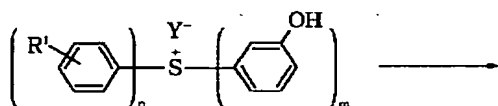
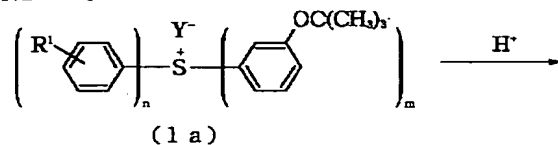
【0047】上記反応においては、上記式(2)のスルホキシドに対して上記式(3)のトリアルキルシリルスルホネートを1～5モル、特に2～3モルの割合で混合することが好適であり、また、上記式(2)のスルホキシドに対して上記式(4)又は上記式(8)のグリニヤ試薬を1～5モル、特に2～3モルの割合で加えることが好ましい。更に、これらの反応は、上記式(3)のトリアルキルシリルスルホネート中に存在する微量の酸性不純物によるtert-ブトキシ基の脱離を防ぐため、トリエチルアミン、ピリジン等の有機塩基の存在下、THF、塩化メチレン等の有機溶媒中で行うことが望ましい。なお、これら反応の反応条件は特に制限されない

が、0～10℃の反応温度とすることが好ましい。

【0048】更に本発明では、上記式(1a)のスルホニウム塩のtert-ブトキシ基を酸により脱保護し、フェノール性水酸基の水素原子を常法によりtert-ブトキシカルボニル基、tert-ブトキシカルボニルメチル基、トリアルキシルシリル基、テトラヒドロピラニル基、メトキシメチル基等の酸不安定基で置換することにより、目的とする酸不安定基をフェニル基の3位に持つ下記一般式(1)で示される新規なスルホニウム塩を得ることができる。

【0049】

【化10】



(但し、上記式中R¹、R²、Y、n、mはそれぞれ上記と同様である。)

【0050】このようにして得られる本発明の上記式(1)の新規なスルホニウム塩は、化学増幅ポジ型レジスト材料の酸発生剤として好適に使用されるもので、この式(1)のスルホニウム塩を酸発生剤として配合し、二成分系(有機溶媒、アルカリ可溶性樹脂、酸発生剤)もしくは三成分系(有機溶媒、アルカリ可溶性樹脂、酸発生剤、溶解阻止剤)の化学増幅ポジ型レジスト材料として調製することができるが、特に三成分系の化学増幅ポジ型レジスト材料として調製することが好適である。

【0051】この場合、酸発生剤としての上記式(1)のスルホニウム塩の配合量は、アルカリ可溶性樹脂100重量部に対し0.5～15部(重量部、以下同様)、特に2～8部とすることが好ましく、0.5部に満たないと露光時の酸発生量が少なく感度及び解像力が劣る場合があり、15部を越えるとレジストの透過率が低下し、解像力が劣る場合がある。

【0052】なお、上記式(1)のスルホニウム塩が配合されたレジスト材料の使用法、光使用法などは公知のリソグラフィ技術を採用して行うことができるが、特に上記レジスト材料は254～193nmの遠紫外光及び電子線による微細パターンニングに最適である。

【0053】

【発明の効果】本発明の上記式(1)の新規なスルホニウム塩は、酸発生剤であるスルホニウム塩のフェニル基の3位に酸不安定基を導入したことにより、露光部と未露光部の溶解コントラストを大きくすることができ、更に3位に酸素原子を導入し、硫黄原子の共鳴構造をとれないようにしたことにより、無置換のトリフェニルホスホニウム塩と同等以上に250nm付近の透過率を高めることができ、その結果レジスト材料としての透過率を高めることができるため、微細加工技術に適した高解像性を有する化学増幅ポジ型レジスト材料の成分として有効である。

【0054】

【実施例】以下、実施例及び比較例、配合例を示して本発明を具体的に説明するが、本発明は下記実施例に制限されるものではない。なお、各例中の部はいずれも重量部である。

【0055】【実施例1】

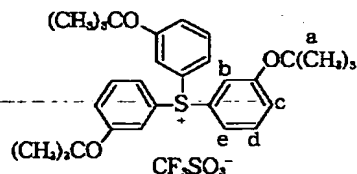
トリフルオロメタンスルホン酸トリス(3-tert-ブトキシフェニル)スルホニウムの合成

ビス(3-tert-ブトキシフェニル)スルホキシド 17.8g(0.052mol)をTHF52gに溶解させ、氷水浴にて冷却した。これにトリエチルアミン 5.3g(0.052mol)を加え、トリメチルシリルトリフルオロメタンスルホネート28.6g(0.13mol)を10℃を越えないようにコントロールしながら滴下し、反応温度を0～10℃として30分間反応の熟成を行った。この溶液に3-tert-ブトキシクロロベンゼン24.0g(0.13mol)と金属マグネシウム3.2g(0.13mol)、THF40gを用いて常法にて調製したグリニヤ試薬を10℃を越えないようにコントロールしながら滴下した。更に、反応温度を0～10℃として反応の熟成を30分間行った。反応液に20%塩化アンモニウム水溶液300gを加えて反応の停止と分液を行った後、有機層にクロロホルム300gを加えた。有機層を水200gを用いて2回水洗した後、溶媒を減圧留去して油状物を得た。この油状物をカラムクロマトグラフィー(シリカゲル：抽出液、クロロホルム-メタノール)にかけたところ、収量10.5g(収率29%)、純度99%のトリフルオロメタンスルホン酸トリス(3-tert-ブトキシフェニル)スルホニウムが単離された。

【0056】得られたトリフルオロメタンスルホン酸トリス(3-tert-ブトキシフェニル)スルホニウムの核磁気共鳴スペクトル(NMR)、赤外スペクトル(IR)、元素分析値及び紫外吸収スペクトル(UV)の結果を下記に示す。なお、比較例としてトリフルオロメタンスルホン酸トリフェニルスルホニウム、トリフルオロメタンスルホン酸トリス(4-tert-ブトキシフェニル)スルホニウムの紫外吸収スペクトルの値も示す。

【0057】

【化11】

¹H-NMR: CDCl₃, δ (ppm)

(a) 1.25

一重項 27H

(b) 7.05~7.06

三重項 3H

(c)、(e) 7.25~7.29

多重項 6H

(d) 7.51~7.57

三重項 3H

IR: (cm⁻¹) 2980, 1587, 1564, 14

理論値 C: 59.2 H: 6.2

77, 1423, 1394, 1369, 1263, 12

分析値 C: 59.1 H: 6.1

59, 1159, 1031, 933, 912, 638.

【0058】

元素分析値: (%) C₂₁H₂₃O₆S₂F₃

【表1】

UV: 紫外吸収スペクトル (メタノール溶液中)

	実施例 1	トリフルオロメタン スルホン酸トリフェ ニルスルホニウム	トリフルオロメタン スルホン酸トリス (4-tert-ブトキシ フェニル) スルホ ニウム
極大吸収 (モル吸光係数)	284nm (6420) 215nm (44100)	233nm (20500) 205nm (47700)	262nm (36700) 207nm (59900)
248nm (モル吸光係数)	(12200)	(14900)	(29000)

【0059】〔実施例2〕実施例1の3-tert-ブトキシフェニルグリニヤの代わりにフェニルグリニヤを用いる以外は実施例1と同様にして反応を行ったところ、トリフルオロメタンスルホン酸ビス(3-tert-ブトキシフェニル)フェニルスルホニウムが純度98%、収率35%で得られた。

【0060】〔実施例3〕実施例1のスルホキシドの代わりにジフェニルスルホキシドを用いる以外は実施例1と同様にして反応を行ったところ、トリフルオロメタンスルホン酸(3-tert-ブトキシフェニル)ジフェニルスルホニウムが純度98%、収率27%で得られた。

【0061】〔実施例4〕実施例1のスルホキシドの代わりにビス(4-ジメチルアミノフェニル)スルホキシドを用いる以外は実施例1と同様にして反応を行ったところ、トリフルオロメタンスルホン酸(3-tert-ブトキシフェニル)ビス(4-ジメチルアミノフェニル)スルホニウムが純度98%、収率27%で得られた。

【0062】〔実施例5〕実施例1のグリニヤ試薬の代わりに4-ジメチルアミノフェニルグリニヤを用いる以外は実施例1と同様にして反応を行ったところ、トリフ

ルオロメタンスルホン酸ビス(3-tert-ブトキシフェニル)(4-ジメチルアミノフェニル)スルホニウムが純度98%、収率33%で得られた。

【0063】〔実施例6~10〕実施例1~5で用いたトリメチルシリルトリフルオロメタンスルホネートの代わりにp-トルエンスルホン酸とトリメチルシリルクロリドとを常法により反応させることで得られるトリメチルシリル-p-トルエンスルホネート(沸点113~117℃/0.5~0.6mmHg)を用いる以外は実施例1~5と同様に反応させたところ、それぞれ下記のようなカウンターアニオンにp-トルエンスルホン酸を持つスルホニウム塩が得られた。

実施例6: p-トルエンスルホン酸トリス(3-tert-ブトキシフェニル)スルホニウム 純度99% 収率35%

実施例7: p-トルエンスルホン酸ビス(3-tert-ブトキシフェニル)フェニルスルホニウム 純度99% 収率28%

実施例8: p-トルエンスルホン酸(3-tert-ブトキシフェニル)ジフェニルスルホニウム 純度99% 収率25%

実施例9: p-トルエンスルホン酸(3-tert-ブ

トキシフェニル) ビス (4-ジメチルアミノフェニル) スルホニウム 純度 97% 収率 31%

実施例 10: p-トルエンスルホン酸ビス (3-tert-ブトキシフェニル) (4-ジメチルアミノフェニル) スルホニウム 純度 98% 収率 32%

【0064】〔実施例 11~15〕実施例 1~5 で用いたトリメチルシリルトリフルオロメタンスルホネートの代わりにノナフルオロブタンスルホン酸とトリメチルシリルクロリドとを常法により反応させることで得られるトリメチルシリルノナフルオロブタンスルホネートを用いる以外は実施例 1~5 と同様に反応させたところ、それぞれ下記のようなカウンターアニオンにノナフルオロブタンスルホン酸を持つスルホニウム塩が得られた。

実施例 11: ノナフルオロブタンスルホン酸トリス (3-tert-ブトキシフェニル) スルホニウム 純度 99% 収率 31%

実施例 12: ノナフルオロブタンスルホン酸ビス (3-tert-ブトキシフェニル) フェニルスルホニウム 純度 99% 収率 28%

実施例 13: ノナフルオロブタンスルホン酸 (3-tert-ブトキシフェニル) ジフェニルスルホニウム 純度 99% 収率 18%

実施例 14: ノナフルオロブタンスルホン酸 (3-tert-ブトキシフェニル) ビス (4-ジメチルアミノフェニル) スルホニウム 純度 98% 収率 27%

実施例 15: ノナフルオロブタンスルホン酸ビス (3-tert-ブトキシフェニル) (4-ジメチルアミノフェニル) スルホニウム 純度 97% 収率 25%

【0065】〔実施例 16~19〕実施例 1~15 で得た tert-ブトキシ基を 3 位に持つ新規なスルホニウム塩をカウンターアニオン (例えばトリフルオロメタンスルホネートや p-トルエンスルホネート) と同じスルホン酸を用いてメタノール又はエタノール中で脱保護

し、対応する 3-ヒドロキシフェニルスルホニウム塩をほぼ定量的に得た後、常法によりジ-tert-ブチルカルボネート、あるいはクロロ酢酸-tert-ブチル、ジヒドロピランを用いることで下記に示すような酸不安定基をフェニル基の 3 位に持つスルホニウム塩を合成した。

実施例 16: ノナフルオロブタンスルホン酸ビス (3-tert-ブトキシカルボニルオキシフェニル) フェニルスルホニウム 純度 98%、収率 23%

10 実施例 17: トリフルオロメタンスルホン酸 (3-tert-ブトキシカルボニルメチルオキシフェニル) ジフェニルスルホニウム 純度 98%、収率 25%

実施例 18: p-トルエンスルホン酸 (3-tert-ブトキシカルボニルオキシフェニル) ジフェニルスルホニウム 純度 98%、収率 19%

実施例 19: ノナフルオロブタンスルホン酸トリス (3-tert-ブトキシカルボニルメチルオキシフェニル) スルホニウム 純度 98%、収率 18%

【0066】上記の実施例 1~10 の新規なスルホニウム塩の 3 位置換体 (3-tert-ブトキシフェニルスルホニウム塩) 及び比較例として 4 位置換体 (4-tert-ブトキシフェニルスルホニウム塩) の 248 nm における紫外吸収スペクトルのモル吸光係数を表 2 に示す。

【0067】表 2 の結果から明らかなように、本発明のスルホニウム塩は、tert-ブトキシ基を 4 位ではなく 3 位に持つことにより 248 nm の光吸収を少なくすることができ、その効果は tert-ブトキシフェニル基の多いトリス (tert-ブトキシフェニル) スルホニウム塩において最も大きく現れることがわかった。

【0068】

【表 2】

UV：紫外吸収スペクトル（メタノール溶媒中）
248nm のモル吸光係数

化 合 物 名	実施例 (3 位置換体)	比較例 (4 位置換体)
トリフルオロメタンスルホン酸トリス (tert-ブトキシフェニル) スルホニウム	12200 (実施例 1)	29000
トリフルオロメタンスルホン酸ビス (tert-ブトキシフェニル) フェニルスルホニウム	13000 (実施例 2)	21000
トリフルオロメタンスルホン酸 (tert-ブトキシフェニル) ジフェニルスルホニウム	13500 (実施例 3)	15500
トリフルオロメタンスルホン酸 (tert-ブトキシフェニル) ビス (4-ジメチルアミノフェニル) スルホニウム	13500 (実施例 4)	15000
トリフルオロメタンスルホン酸ビス (tert-ブトキシフェニル) (4-ジメチルアミノフェニル) スルホニウム	14000 (実施例 5)	21000
p-トルエンスルホン酸トリス (tert-ブトキシフェニル) スルホニウム	12500 (実施例 6)	28000
p-トルエンスルホン酸ビス (tert-ブトキシフェニル) フェニルスルホニウム	13300 (実施例 7)	20500
p-トルエンスルホン酸 (tert-ブトキシフェニル) ジフェニルスルホニウム	14000 (実施例 8)	15800
p-トルエンスルホン酸 (tert-ブトキシフェニル) ビス (4-ジメチルアミノフェニル) スルホニウム	14000 (実施例 9)	15000
p-トルエンスルホン酸ビス (tert-ブトキシフェニル) (4-ジメチルアミノフェニル) スルホニウム	14500 (実施例 10)	20000

【0069】〔配合例1～14、比較配合例1～5〕表3、4に示すように下記式（Polym. 1）で示される部分的に水酸基の水素原子をtert-ブトキシカルボニル基で保護したポリヒドロキシスチレン、下記式

（Polym. 2）で示される部分的に水酸基の水素原子をtert-ブチル基で保護したポリヒドロキシスチレン又は下記式（Polym. 3）で示される部分的に水酸基の水素原子をテトラヒドロピラニル基で保護したポリヒドロキシスチレンと、下記式（PAG. 1）から（PAG. 5）で示されるオニウム塩から選ばれる酸発生剤と、下記式（DRI. 1）で示される2, 2'-ビス（4-tert-ブトキシカルボニルオキシフェニル）プロパンの溶解阻止剤を1-エトキシ-2-プロパノールに溶解し、表3に示す各種組成のレジスト組成物を調製した。

【0070】得られたレジスト組成物を0.2μmのテフロン製フィルターで濾過することによりレジスト液を調製した後、このレジスト液をシリコンウェハー上へスピンコーティングし、0.8μmに塗布した。

【0071】次いで、このシリコンウェハーを100℃のホットプレートで120秒間ベークした。更に、エキシマレーザーステッパー（ニコン社、NSR2005 EXNA=0.5）を用いて露光し、90℃で60秒間ベークを施し、2.38%のテトラメチルアンモニウムヒドロキシドの水溶液で現像を行うと、ポジ型のパターンを得ることができた。

【0072】得られたレジストパターンを次のように評価した。結果を表3、4に示す。

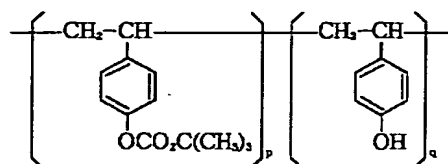
レジストパターン評価方法：まず、感度（Eth）を求めた。次に、0.35μmのラインアンドスペースのトップとボトムを1：1で解像する露光量を最適露光量（感度：Eop）として、この露光量における分離しているラインアンドスペースの最小線幅を評価レジストの解像度とした。また、解像したレジストパターンの形状は、走査型電子顕微鏡を用いて観察した。

【0073】

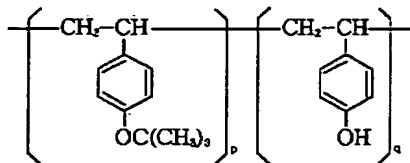
【化12】

23

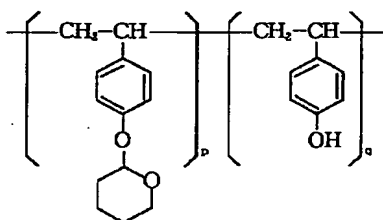
24



Polym.1



Polym.2



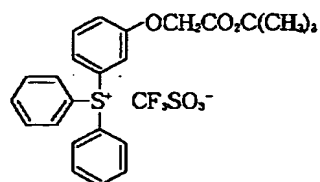
Polym.3

$p/(p+q)=0.1\sim0.3$
重量平均分子量 10,000~50,000

【 0 0 7 4 】

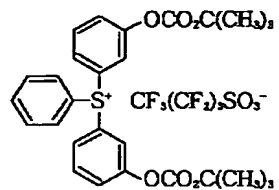
【 化 1 3 】

25

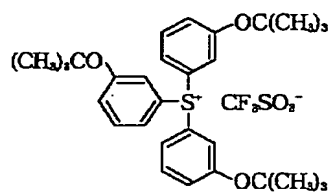


PAG.1

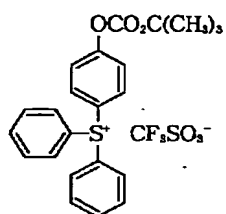
26



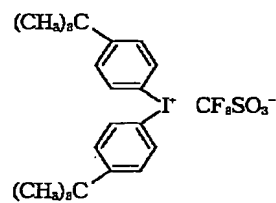
PAG.2



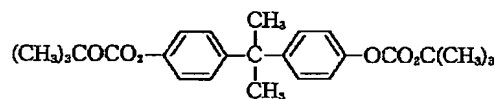
PAG.3



PAG.4



PAG.5



DRI.1

【 0 0 7 5 】

【 表 3 】

配合例	レジスト組成物〔括弧内：組成比（単位：重量部）〕				感度 :Eop (mJ/cm ²)	解像度 (μm)	パターン 形状
	アルカリ可 溶性樹脂	酸発生剤	溶解阻止剤	溶媒			
1	Polym.1 (75)	PAG.1 (5)	DRL1 (20)	EtOIPA (450)	4.5	0.24	矩形
2	Polym.1 (75)	PAG.2 (5)	DRL1 (20)	EtOIPA (450)	4.5	0.24	矩形
3	Polym.1 (75)	PAG.3 (5)	DRL1 (20)	EtOIPA (450)	5.0	0.22	矩形
4	Polym.1 (70)	PAG.1 (2) PAG.4 (2)	DRL1 (20)	EtOIPA (450)	4.5	0.26	矩形
5	Polym.1 (70)	PAG.3 (2) PAG.5 (2)	DRL1 (20)	EtOIPA (450)	5.5	0.28	矩形
6	Polym.1 (75)	PAG.3 (6)	—	EtOIPA (450)	6.0	0.26	矩形
7	Polym.1 (75)	PAG.3 (3) PAG.5 (2)	—	EtOIPA (450)	6.0	0.30	矩形
8	Polym.2 (75)	PAG.1 (5)	DRL1 (20)	EtOIPA (450)	5.0	0.24	矩形
9	Polym.2 (75)	PAG.3 (5)	DRL1 (20)	EtOIPA (450)	6.0	0.24	矩形
10	Polym.2 (70)	PAG.2 (2) PAG.5 (2)	DRL1 (20)	EtOIPA (450)	6.0	0.28	矩形
11	Polym.2 (75)	PAG.3 (5)	—	EtOIPA (400)	6.5	0.30	矩形
12	Polym.3 (75)	PAG.1 (5)	DRL1 (20)	EtOIPA (450)	6.0	0.26	矩形
13	Polym.3 (75)	PAG.3 (5)	DRL1 (20)	EtOIPA (450)	6.5	0.24	矩形
14	Polym.3 (75)	PAG.2 (2) PAG.5 (2)	DRL1 (20)	EtOIPA (400)	6.5	0.28	矩形

EtOIPA：1-エトキシ-2-プロパノール

【0076】

【表4】

比較 配合例	レジスト組成物〔括弧内：組成比（単位：重量部）〕				感度 :Eop (mJ/cm ²)	解像度 (μm)	パターン 形状
	アルカリ可 溶性樹脂	酸発生剤	溶解阻止剤	溶媒			
1	Polym.1 (75)	PAG.4 (5)	DRL1 (20)	EtOIPA (450)	4.0	0.28	若干順テーバー
2	Polym.2 (75)	PAG.5 (5)	DRL1 (20)	EtOIPA (450)	4.0	0.30	若干順テーバー
3	Polym.3 (75)	PAG.5 (5)	DRL1 (20)	EtOIPA (450)	4.0	0.30	順テーバー
4	Polym.1 (80)	PAG.4 (6)	—	EtOIPA (400)	5.0	0.30	順テーバー

【0077】〔配合例15～28、比較配合例5～8〕

表5、6に示すように酸発生剤として下記（PAG. 6～8）又は上述した（PAG.4、5）を用いる以外は上記配合例1と同様にしてポジ型パターンを得た。なお、

配合例28にはPED安定性のための窒素含有化合物を添加剤として加えた。

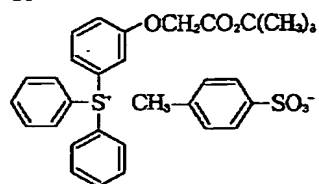
【0078】得られたレジストパターンを上記と同様に評価した。更に、レジストのPED安定性は、最適露光

量で露光後、放置時間を変えてPEBを行い、レジストパターン形状の変化が観察された時間、例えばラインパターンがT-トップとなったり、解像できなくなった時間で評価した。この時間が長いほどPED安定性に富む。以上の結果を表5、6に示す。

【0079】

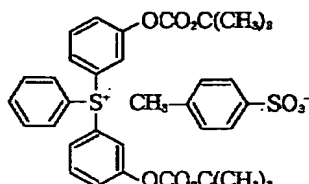
【化14】

29

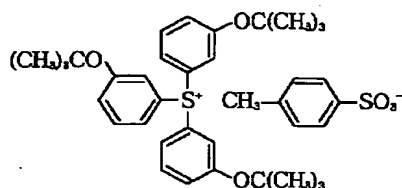


PAG.6

30



PAG.7



PAG.8

【0080】

【表 5】

配合例	レジスト組成物 (括弧内: 組成比 (単位: 重量部))					感 度 : E _{0p} (mJ/cm ²)	解像度 (μm)	パター ン形状	PED 安定性 (分)
	アルカリ 可溶性樹脂	酸発生剤	溶解阻止剤	窒素含有 化合物	溶 媒				
15	Polym.1 (80)	PAG.6 (5)	DRL1 (20)	-	EtOIPA (450)	14.0	0.24	矩形	60 以上
16	Polym.1 (80)	PAG.7 (5)	DRL1 (20)	-	EtOIPA (450)	16.0	0.24	矩形	60 以上
17	Polym.1 (80)	PAG.8 (5)	DRL1 (20)	-	EtOIPA (450)	19.0	0.22	矩形	60 以上
18	Polym.1 (75)	PAG.8 (2) PAG.4 (2)	DRL1 (20)	-	EtOIPA (500)	12.0	0.28	矩形	30 以上
19	Polym.1 (75)	PAG.8 (5)	-	-	EtOIPA (500)	20.0	0.24	矩形	60 以上
20	Polym.1 (75)	PAG.7 (2) PAG.5 (2)	-	-	EtOIPA (500)	13.0	0.28	矩形	30 以上
21	Polym.2 (70)	PAG.8 (5)	DRL1 (20)	-	EtOIPA (450)	13.0	0.25	矩形	30 以上
22	Polym.2 (70)	PAG.8 (5)	DRL1 (20)	-	EtOIPA (450)	17.0	0.25	矩形	30 以上
23	Polym.2 (70)	PAG.8 (3) PAG.4 (2)	DRL1 (10)	-	EtOIPA (400)	17.5	0.28	矩形	30 以上
24	Polym.2 (75)	PAG.8 (5)	-	-	EtOIPA (450)	18.0	0.25	矩形	30 以上
25	Polym.3 (70)	PAG.8 (5)	DRL1 (20)	-	EtOIPA (450)	18.0	0.26	矩形	30 以上
26	Polym.3 (70)	PAG.6 (3) PAG.4 (2)	DRL1 (10)	-	EtOIPA (400)	17.0	0.30	矩形	30 以上
27	Polym.3 (75)	PAG.8 (5)	-	-	EtOIPA (450)	21.0	0.28	矩形	30 以上
28	Polym.1 (80)	PAG.8 (5)	DRL1 (20)	NMP (0.1)	EtOIPA (450)	28.0	0.22	矩形	90 以上

EtOIPA: 1-エトキシ-2-プロパノール

NMP: N-メチルピロリドン

【0081】

【表 6】

比較 配合例	レジスト組成物 (括弧内：組成比 (単位：重量部))				感 度 :Eop (mJ/ cm ²)	解像度 (μ m)	パター 形状	PED 安定性 (分)
	アルカリ可 溶性樹脂	酸発生剤	溶解阻止剤	溶 媒				
5	Polym.1 (75)	PAG.4 (5)	DRL1 (20)	EtOIPA (450)	4.0	0.28	若干順 テーパー	5以下
6	Polym.2 (75)	PAG.5 (5)	DRL1 (20)	EtOIPA (450)	4.0	0.30	若干順 テーパー	5以下
7	Polym.3 (75)	PAG.5 (5)	DRL1 (20)	EtOIPA (450)	4.0	0.30	順テーパー	5以下
8	Polym.1 (80)	PAG.4 (6)	-	EtOIPA (400)	5.0	0.30	順テーパー	5以下

フロントページの続き

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